A Numerical Approach to the Accurate Calculation of Atomic and Molecular Properties

by

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Abstract: A Numerical Approach to the Accurate Calculation of Atomic and Molecular Properties.

An attempt is made to demonstrate that simple numerical methods can be used to advantage in the accurate calculation of atomic and molecular properties.

In the early part of the thesis finite-difference techniques are employed in conjunction with conventional variational methods to cal--culate accurately the correlation energies of small atoms within a variety of perturbation schemes. Of particular interest is a thorough investigation of Hartree-Fock perturbation theory through third order for the Be isoelectronic sequence Li^- — Ne^{6+} with about a 90% recovery of E_{corr}.

Numerical methods are also used to examine the efficacy of the single-centre approach to the calculation of the electronic structures of simple molecules in their ground and excited states, the high accuracy of the computational scheme employed allowing some insight into the frequently observed slow convergence of the one-centre method.

The efficiency of numerical techniques in the determination of atomic and molecular properties is further shown by studies on the non-empirical evaluation of atomic polarisabilities (static and dynamic) and of interatomic dispersion forces. Notably a new method of computing Van der Waals coefficients of considerable elegance and economy is presented.

In the final section of the work the numerical computational techniques developed in non-empirical calculations of pair correlation energies, polarisabilities, dispersion coefficients in small systems are applied to much larger atoms within a model potential framework. All of the above properties are determined for a wide variety of systems with however the alkali metals and their anions being the subject of the most comprehensive treatment.

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CONTENTS

Chapter 1 An Introduction.

1.1 Purpose and development of this work

A Purpose

The purpose of this work is to demonstrate that simple numerical methods can be used to advantage in the accurate calculation of atomic and molecular properties.

B Scope

The initial motivation for this work was the recent introduc-tion into chemical physics by McKoy, Winter and co-workers* of finite-difference methods to solve the elliptic partial differential equations arising in the accurate treatment of correlation in two-electron systems. As these authors point out such techniques are extremely useful when used in conjunction with modern computing equipment since their application involves the execution of a huge number of very simple (and hence easily coded) operations. In addition both the theory and practice of such methods have been extensively researched. To start with the objective of this research programme was thus to examine further the possible use of a finite-difference method of attack on the correlation problem in small atomic systems. However after a substantial measure of success had been achieved in this direction it was decided to enlarge the scope of the investigation beyond its rather narrowly defined field to the more general consideration of the evaluation of certain properties of atoms and molecules,

* See for example references (M5, W12, W13, W14, W15, W17, W18).

particularly those calculable by low order perturbation theory. At this point it may be observed that while in the discipline of engineering the numerical techniques referred to above have been frequently employed, their application in theoretical chemistry appears in the author's opinion to have been curiously neglected. Before proceeding two simple examples will perhaps illustrate the possible justification of this viewpoint and set the background for the general body of the thesis.

1.2 An illustrative example The interaction of a hydrogen atom with a point charge.

Consider a hydrogen atom perturbed by a point charge placed at a distance R from it. The perturbation can be expanded as shown in (1) and the first order correction to the wavefunction evaluated from the perturbation equation (2). Atomic units are used here as throughout the whole work unless otherwise stated.

$$H' = -\frac{1}{R}\sum_{\ell=1}^{\infty}\left(\frac{r}{R}\right)^{\ell} P_{\ell}(\cos\Theta) \qquad (1)$$

$$(H^{\circ} - E^{\circ})\,\psi' = (E1 - H')\,\psi^{\circ} \qquad (2)$$

Here (2) has a simple analytical solution (3) and the second order energy can be written in inverse powers of R as in (4).*

* The solution can be found in most elementary textbooks such as (S4).

$$\underline{\psi}' = \sum_{\ell=1}^{\infty} R^{-(\ell+1)} \left(\frac{r}{\ell} + \frac{r^{(\ell+1)}}{(\ell+1)}\right) \exp(-r)\, P_\ell(\cos\Theta) \qquad (3)$$

$$E2 = \sum_{n} B_n R^{-n} = -\sum_{\ell=1}^{\infty} \frac{(\ell+2)\,(2\ell+1)!}{\ell\, 2^{2\ell+1}} R^{-(2\ell+2)} \qquad (4)$$

In the absence of the extremely fortuitous circumstance of knowing (3) it may be asked how the inhomogeneous differential equation (2) might be solved so as to give the second order energy to a reasonable degree of accuracy? Firstly ψ' is expressed in the form (5) and with suitable manipulation and integration over the angular variables a set of radial equations each of the type (6) is obtained.

$$\psi' = \sum_{\ell=1}^{\infty} (\pi)^{-\frac{1}{2}} r^{-1} f_\ell(r)\, P_\ell(\cos\Theta) \qquad (5)$$

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - r^{-1} + 0.5\right) f_\ell(r)$$

$$= r^{(\ell+1)} \exp(-r)\, R^{-(\ell+1)} \qquad (6)$$

Now the second derivative term can be expressed by a simple difference formula such as (7), h being the spacing of the grid on which the equation is approximated.

$$f''(r_o) \approx h^{-2} (f(r_o+h) - 2f(r_o) + f(r_o-h)) \qquad (7)$$

It is thus evident that (2) can be transformed into sets of linear equa--tions for the values of the components of the first order wavefunction at the grid points. If the second difference approximation (7) is used the coefficient matrix om the L.H.S. of the analogue of (6) is tridiagonal and an elementary algorithm can be employed for the solution of the equa--tions.*

For the boundary conditions the simplest possibility is taken viz. that f(r) vanishes at a suitably large distance from the nucleus.

At this point it might be anticipated that the numerical function could be a poor approximation to the exact solution and hence furnish an unsatisfactory result for E2. However there is a way to improve greatly upon the primitive values of the B_n:- If calculations are carried out for a series of different grid spacings then it is possible to exploit the fact that the approximate B_n for a given h is expressible as a power series in even powers of h, $B_n(0)$ being the desired exact result in the formula (8).

$$B_n(h) = B_n(0) + C_2 h^2 + C_4 h^4 + C_6 h^6 \ldots\ldots\ldots \qquad (8)$$

This process, known as Richardson extrapolation, has been discussed by Richardson and Gaunt (R2) and by Bolton and Scoins (B11).

* See for example (V1) page 195 for a statement of the algorithm.

In Tables 1.1 and 1.2 some results are detailed for the lead--ing term B_4 of E2, the only difference in the calculations from the des--cription given above being a scale transformation $r = x^2$ to give a slightly more favourable distribution of the grid points. For each calcul--ation the primitive values are placed on the L.H.S. and the succeeding columns correspond to extrapolants from the appropriate 3,4 or 5 such results. Some features can be noticed immediately:- Firstly while the unextrapolated values are generally of only moderate accuracy the extra--polants give quite excellent agreement with the exact results -2.25 a.u.. Secondly the use of too small a radial cutoff somewhat diminishes the accuracy of the calculation but however the latter is maintained even if the boundary is placed somewhat further out than is strictly necessary. Finally it can be seen that it is not an advantage to use very large numbers of grid points, the build-up of rounding error in the extrapolation of the last set of results being obvious. Indeed, as can be seen from the penultimate group of calculations, the use of modest numbers of strips gives very accurate extrapolants while the computational effort is much less.

The above problem is certainly of a very simple type and it may be felt that the approach detailed above for its solution cannot be generalised to more complicated situations. As a first attempt to resolve this question the coefficients of odd powers of R^{-1} for the above problem, which arise in third order of perturbation theory, are given in Table 1.3 having been computed from the various components of the first order wavefunction and extrapolated as before. Again the results are most grat--ifying, the only major requirement being the use of a sufficiently gene--rous cutoff. Hence this suggests that the procedure may be successful for the evaluation of many properties of the first order perturbed wave-function thus considerably widening the scope of the approach.

Table 1.1 Results for the perturbation of a hydrogen atom by a point charge:- B_4 coefficient calculated from various grids and radial cutoffs.

Grid sizes are 100, 200, 300, 400, 500 strips. Cutoff is 20.0 a.u..

-2.25047293			
-2.25011821	-2.25000000		
		-2.25000000	
-2.25005254	-2.25000000		-2.25000000
		-2.25000000	
-2.25002955	-2.25000000		
-2.25001891			

Grid sizes are 100, 200, 300, 400, 500 strips. Cutoff is 10.0 a.u..

-2.24932591			
-2.24915155	-2.24909344		
		-2.24909344	
-2.24911927	-2.24909344		-2.24909343
		-2.24909343	
-2.24910797	-2.24909344		
-2.24910274			

Grid sizes are 100, 200, 300, 400, 500 strips. Cutoff is 15.0 a.u.

-2.25035424			
-2.25008823	-2.24999957		
		-2.24999957	
-2.25003897	-2.24999957		-2.24999957
		-2.24999957	
-2.25002173	-2.24999957		
-2.25001376			

Table 1.2 Results for the perturbation of a hydrogen atom by a point charge:- B_4 coefficient calculated from various grids and radial cutoffs.

Grid sizes are 100, 200, 300, 400, 500 strips. Cutoff is 35.0 a.u..

-2.25082778			
-2.25020688	-2.25000000		
		-2.25000000	
-2.25009194	-2.25000000		-2.25000000
		-2.25000000	
-2.25005172	-2.25000000		
-2.25003310			

Grid sizes are 60, 70, 80, 90, 100 strips. Cutoff is 20.0 a.u..

-2.25131425			
-2.25096540	-2.25000000		
		-2.25000000	
-2.25073905	-2.25000000		-2.25000000
		-2.25000000	
-2.25058390	-2.25000000		
-2.25047293			

Grid sizes are 460, 470, 480, 490, 500 strips. Cutoff is 20.0 a.u..

-2.25002234			
-2.25002140	-2.25000032		
		-2.24999336	
-2.25002052	-2.24999950		-2.25007322
		-2.25000563	
-2.25001969	-2.25000021		
-2.25001891			

Table 1.3 The coefficients of the odd powers of R^{-1} for the multipole expansion of the interaction of H with a point charge com-
-puted for various radial cutoffs.

Cutoff	R^{-7}	R^{-9}	R^{-11}
10.0	-52.835021	-857.79528	-19219.071
15.0	-53.249372	-886.40380	-21203.122
20.0	-53.250000	-886.49990	-21217.475
25.0	-53.250000	-886.50000	-21217.500
30.0	-53.250000	-886.50000	-21217.500
50.0	-53.250000	-886.50000	-21217.500

Exact values for the above coefficients are -213/4, -1773/2, and -42435/2 (see H.Kreek and W.J.Meath, reference (K15)).

1.3 A second illustrative example The interaction of two hydrogen atoms at long range.

In 1.2 a problem involving only one radial dimension was resolved using numerical methods, it being now useful to demonstrate the application of such techniques to a calculation involving two dimensions. For this purpose the problem of the interaction of two ground state hydrogen atoms at long rage will be considered.

The Hamiltonian for the system can be written as (9), the per--turbation being (11) where the M_{ij} and θ_{ij} are defined as in Kolos (K14).

$$H = H^{o} + H' \tag{9}$$

where

$$H^{o} = h^{o}(a1) + h^{o}(b2) \tag{10}$$

and

$$H' = \sum_{i,j} 4\pi M_{ij}\, r_{a1}^{i}\, r_{b2}^{j}\, R^{-(i+j+1)}\, \theta_{ij} \tag{11}$$

Now again a solution of the first order perturbation equation (2) permits the evaluation of E2 in the well-known series (12) with here n commencing at six.

$$E2 = \sum_{n} B_{n} R^{-n} \tag{12}$$

Conversion of (2) into a form suitable for the application of numerical techniques is very easily accomplished. For the first term in the series

the requisite part of the first order wavefunction is of the form (13) which, on substitution in the perturbation equation, gives rise to the elliptic partial differential equation (14).

$$\Phi^{1} = U_{11}(r_{a1},r_{b2})\ \theta_{11}\ R^{-3} \tag{13}$$

$$\left(-\tfrac{1}{2}\left(\frac{1}{r_{a1}^{2}} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^{2} \frac{\partial}{\partial r_{a1}} \right) + \frac{1}{r_{b2}^{2}} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^{2} \frac{\partial}{\partial r_{b2}} \right) \right) + r_{a1}^{-2} + r_{b2}^{-2} \right.$$

$$\left. - r_{a1}^{-1} - r_{b2}^{-1} + 1.0 \right) U_{11}(r_{a1},r_{b2}) = 4.0\ M_{11}\ r_{a1}\ r_{b2}\ \exp(-r_{a1}-r_{b2}) \tag{14}$$

Such an equation can be straightforwardly solved using finite-difference methods as was the one-dimensional problem discussed in 1.2. Taking $G_{11}(r_{a1},r_{b2}) = r_{a1}r_{b2}\ U_{11}(r_{a1},r_{b2})$ then employing a fourth difference approximation for the second derivative terms, changing to a second difference formula at the boundaries, G_{11} is found in the square region $(0 \leqslant r_{a1} \leqslant R_{max}\ ,\ 0 \leqslant r_{b2} \leqslant R_{max})$. R_{max} is the cutoff radius beyond which the radial function is assumed to vanish, here 35.0 a.u. being found suitable. The linear equations were solved by Successive OverRelaxation (SOR) on a 'square root' grid using between 20 and 50 strips in each dimension.

Extrapolation tables for the dipole-dipole and quadrupole-quadrupole coefficients are given in Table 1.4 along with the essentially exact values of Deal (D11). It can be observed that these terms have been evaluated such that the error in each one is less than one part in 100 000 000, an accuracy which is considered to be more than sufficient for most purposes. One may note that Deal's approach is a

Table 1.4 The extrapolation tables for the finite-difference calculation of the dipole-dipole and quadrupole-quadrupole terms in the long-range energy expansion for two ground state H atoms. The calculations were carried out for 20(5)50 strips with a radial cutoff of 35.0 a.u..

Dipole-dipole term

-6.50662097			
-6.50233238	-6.49859793		
-6.50066307		-6.49903125	
-6.49992158	-6.49898779		-6.49902665
-6.49955512		-6.49902686	
-6.49935808	-6.49902017		
-6.49924477			

Quadrupole-quadrupole term

-1135.94036			
-1135.52205	-1135.19514		
-1135.36557		-1135.21399	
-1135.29685	-1135.21121		-1135.21404
-1135.26298		-1135.21404	
-1135.24477	-1135.21338		
-1135.23429			

The essentially exact values of Deal (D11) for the above quantities are -6.4990267054_0 and -1135.2140398_97.

tour de force which cannot be extended to the evaluation of dispersion coefficients in more generalised systems, a restriction which does not apply to the numerical method as will be seen when this topic is returned to in Chapters 6 and 8.

1.4 An outline of the thesis

In the two examples described beforehand it has been seen how very simple finite-difference techniques can be used to solve resp--ectively a one-dimensional and a two-dimensional inhomogeneous differ--ential equation arising in perturbation theory. For the two problems either the exact solution or an excellent approximation to it were known, this however being an extremely rare situation in quantum chemistry as the reader will appreciate. In the body of this work an attempt will be made to solve analogous problems of chemical and physical interest for which no exact solutions have as yet been found.

In Chapter 2 the elliptic partial differential equations arising from the treatment of the correlation problem in two-electron atoms will be considered. Numerical methods will be used in conjunction with more conventional variational approaches for a study of the applic--ation of several types of perturbation scheme through low order to two-electron atoms in their ground and excited S states. The general--isation of this approach in given in Chapter 3 for the four-electron sequence employing a Hartree-Fock framework for the perturbation theory. In this section preliminary calculations on the Ne sequence will also be described.

In the fourth Chapter eigenvalue problems will be invest--igated for the first time in this work when the calculation of one-centre

wavefunctions for the ground and excited states of simple molecular systems such as H_2^+ will be under study. In particular it is intended to suggest conditions in which the single-centre approach may be competitive with multi-centre methods.

Problems of the type 1.2 and 1.3, involving the calculation of a property through first order perturbation theory in the wavefunction, will be tackled in Chapters 5 and 6. In the first of these the evaluation of static and dynamic polarisabilities in light atoms will be covered in depth within a variety of approximations. The second describes the means by which dispersion coefficients can be found accurately using numerical techniques.

The approaches used above are non-empirical in nature i.e. there are for example no arbitrary parameters in the Hamiltonian which are then determined so as to reproduce experimental values of a certain property, say the energy. However although non-empirical methods gener--ally give fairly accurate values for many properties they are usually unsuitable for other than small systems as the computational effort otherwise becomes excessive. For larger systems semi-empirical techn--iques are required and thus in 7 and 8 the use of the pseudo or model potential method for the calculation of atomic multipole polarisabilities and long-range interactions will be examined.

Finally in Chapter 9 the model potential method referred to above will be utilised to try to give accurate estimates of the valence pair energies in medium and large atoms notably the negative ions of the alkali metals.

In the last section of this thesis it is hoped to briefly summarise the principal achievements and failures of this work although much of this will be done at the end of each Chapter. Indeed it is intended that each segment should be as self-contained as possible for

easier reading and to convey the relevance of the work performed here to that of other workers on the specific topic. Thus most Chapters will have their own sections on for example theory or the historical develop--ment of the problem, but however references are global and are listed at the end of the thesis. Before proceeding to the next Chapter it may lastly be remarked that it will be attempted at several stages to give a realistic projection of possible future progress in the solution of certain of the problems discussed in this work. It is hoped that the reader will perhaps find this, to no matter how small an extent, an assistance in his own study hereafter.

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Chapter 2 Some Studies of Correlation in Two-Electron Atoms Using Perturbation Theory.

2.1 Introduction

In this Chapter the problem of correlation in two-electron atomic systems will be investigated with a variety of zeroth Hamiltonians being used in perturbation studies through third order in the energy. As previously stated the initial motivation for this work was the recent researches of McKoy, Winter and co-workers, these authors using only numerical methods in their studies of the isoelectronic sequence within both perturbation and non-perturbation schemes (M5, W12, W13, W14, W15, W17, W18). However here it is intended to demonstrate that a combination of numerical techniques and conventional variational methods is perhaps the most satifactory means of accomplishing the perturbation calculations.

In section 2.2 calculations on the ground state of the series employing hydrogenic and screened hydrogenic Hamiltonians will be descr--ibed in considerable detail, with emphasis on the numerical procedures which were examined, as similar approaches will be used extensively throughout the Chapter and elsewhere in the Thesis. Following this the excited $^{1,3}S$ states of the series through to 1S5S $^{1,3}S$ will be briefly dealt with, again within a framework of hydrogenic perturbation theory. Also in 2.3 the convergence of the partial wave components of E2 will be discussed with the intention of verifying Schwartz's conjecture that this will be as ℓ^{-4} and ℓ^{-6} for the singlet and triplet states respect--ively (S10).

Hartree and Hartree-Fock theories will be used in 2.4 and 2.5 while in 2.6 a novel form of perturbation theory utilising the S

limit wavefunction as the zero order basis will be developed. The first two are of considerable importance as they correspond to the V^{N-1} and Hartree-Fock Hamiltonians in many-electron systems, but the latter is something of a curiousity which however sheds some light on the import--ance of radial and angular components of the correlation energy.

Finally in 2.7 total energies for the isoelectronic sequence from H^- through to Ne^{8+} evaluated using the various approaches will be compared with each other and with the exact non-relativistic values. From this it will be seen that even for such simple systems it is in general not possible to say a priori which type of perturbation theory will give the fastest convergence.

2.2 Hydrogenic and screened hydrogenic treatment of the ground state

A Theory

In the simplest possible perturbation scheme for the two-electron atom the seroth Hamiltonian and wavefunction can be rep--resented in the hydrogenic form (1) and (2) with the electron interaction as the perturbation (3).

$$H^o = \sum_{i=1}^{2} h^o(i) = -\tfrac{1}{2}\nabla_1^2 - Z/r_1 - \tfrac{1}{2}\nabla_2^2 - Z/r_2 \qquad (1)$$

$$\psi^o = \Phi_{1s}(1)\ \Phi_{1s}(2)\ 2^{-\frac{1}{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \qquad (2)$$

$$H' = r_{12}^{-1} \qquad (3)$$

Now if the energy and radial distances are scaled suitably in units of Z^2 and Z^{-1} then the energy and wavefunction can be written as (4) and it is only necessary to perform one calculation to determine the energy of the system for any desired Z.

$$E = E0 + E1/Z + E2/Z^2 + E3/Z^3 \ldots\ldots\ldots\ldots$$

$$\Psi = \psi^0 + \psi^1/Z + \psi^2/Z^2 \ldots\ldots\ldots\ldots\ldots\ldots \qquad (4)$$

Another obvious choice for H^0 is a sum of screened hydrogenic single-particle operators (5) and again with an appropriate selection of units the energy of any member of the isoelectronic sequence can be evaluated from a single set of E_n.

$$h^0(i) = -\tfrac{1}{2}\nabla_i^2 - (Z-\sigma)/r_i \qquad (5)$$

For the systems under discussion the first order perturbation equation (6) involves of course six different electron co-ordinates. Immediate integration over the Euler angles could be carried out to leave an equation involving r_1, r_2 and r_{12} or transformed combinations of these. However it is felt that the accurate solution of three-dimensional prob-lems is not really a feasible proposition given present computing equip-ment, the attempt by Barraclough and Mooney (B3) to solve exactly for the helium ground state wavefunction, although certainly a valuable

first step in this direction, requiring a huge computational effort. Instead the first order wavefunction is expanded in a Legendre series in the intervector angle θ_{12} as below in (8).

$$(H^{o} - E^{o})\psi^{1} = (E1 - H^{1})\psi^{o} \tag{6}$$

where

$$E1 = \langle \psi^{o} | H^{1} | \psi^{o} \rangle \tag{7}$$

$$\psi^{1} = \sum_{l=0}^{\infty} (4\pi)^{-1} U_{l}(r_1, r_2) P_{l}(\cos \theta_{12}) \tag{8}$$

The result of this is to replace the three-dimensional problem with an infinite series of more tractable two-dimensional equations on substi--tution of (8) into (6) and integration over the angular variables. For each partial wave it is required that an elliptic partial differential equation (9) be solved,* E2 being given by the sum of partial wave contributions (10). E3 is however not diagonal in the U_l but can be evaluated from the expression (11).

$$\left(-\tfrac{1}{2}\left(r_1^{-2} \frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1}\right) + r_2^2 \frac{\partial}{\partial r_2}\left(r_2^2 \frac{\partial}{\partial r_2}\right)\right) + \frac{l(l+1)}{2}\left(r_1^{-2} + r_2^{-2}\right) \right.$$

$$\left. - r_1^{-1} - r_2^{-1} + 0.5 + 0.5 \right) U_l(r_1, r_2)$$

$$= \left(0.625\, \delta_{l0} - \frac{r_<^{l}}{r_>^{l+1}}\right) R_{1s}(r_1)\, R_{1s}(r_2) \tag{9}$$

* Here the relevant equations for the hydrogenic Hamiltonian are given.

$$E2 = \sum_{\ell} \varepsilon 2(\ell)$$

$$= \sum_{\ell} (2\ell+1)^{-1} \int U_{\ell}(r_1,r_2) \left(\frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} - 0.625\ \delta_{\ell o} \right) R_{1s}(r_1)\ R_{1s}(r_2)$$

$$\times\ r_1^2\ r_2^2\ dr_1\ dr_2 \qquad (10)$$

$$E3 = \sum_{\ell,\ell',k} C^k(\ell,\ell') \int U_{\ell}(r_1,r_2)\ \frac{r_{<}^{k}}{r_{>}^{k+1}}\ U_{\ell'}(r_1,r_2)\ r_1^2\ r_2^2\ dr_1\ dr_2$$

$$- E1 \sum_{\ell} (2\ell+1)^{-1} \int U_{\ell}^2(r_1,r_2)\ r_1^2\ r_2^2\ dr_1\ dr_2$$

$$- 2.0 \times E2 \int U_o(r_1,r_2)\ R_{1s}(r_1)\ R_{1s}(r_2)\ r_1^2\ r_2^2\ dr_1\ dr_2 \qquad (11)$$

where

$$C^k(\ell,\ell') = (1+\delta_{\ell\ell'})^{-1} \int P_{\ell}(\cos\theta_{12})\ P_{k}(\cos\theta_{12})\ P_{\ell'}(\cos\theta_{12})\ d(\cos\theta_{12}) \qquad (12)$$

B Methods of solution of the differential equations

Until McKoy and Winter (M5, W17) demonstrated that finite-difference techniques could be used for such a purpose equations of the type (9) were usually solved by variational methods based on the funct--ional (13). Here a combination of these two approaches is used for reasons which are described below:-

$$F(\psi_t') = \langle \psi_t' | H^o - E^o | \psi_t' \rangle + 2 \langle \psi_t' | H' - E1 | \psi^o \rangle \qquad (13)$$

As is known from for example the work of Byron and Joachain (B19) the S wave ($\ell = 0$) component of ψ' can be represented by a linear combination of simple functions of the form say (14) (which the above call a 'CI' type) to a high degree of accuracy.

$$\Phi = (r_1^m r_2^n + r_1^n r_2^m)(\exp(-\alpha r_1 - \beta r_2) + \exp(-\alpha r_2 - \beta r_1)) \qquad (14)$$

However as ℓ increases it becomes extremely difficult to maintain prec-ision and it is interesting to note Schwartz's comment on the higher partial waves that "For high ℓ values the most important part of this function is concentrated very sharply about the point $r_1 = r_2$ and a direct attack on the associated two dimensional partial differential equations might be the best way to solve for these highly correlated functions" (S10). Now if finite-difference methods are used to solve (9) it is found that some difficulty is encountered for the S wave due to the very large number of linear equations which are required to be solved. For the other partial waves methods such as the Gauss-Seidel technique can be used but for the $\ell = 0$ component, since the coefficient matrix on the L.H.S. is not diagonally dominant, divergence is found for the iterative methods.* Thus A Direct method such as Gaussian elimination is needed with the consequent disadvantages of enormous storage problems, reduced stability to rounding error, larger processing time and so on. It may also be noted that the difference formulae, boundary conditions and other characteristics which yield the best results are apparently

* Divergence for the S wave was not always encountered in this type of calculation. However it is common enough to merit consideration of other means of tackling the problem.

somewhat different for the S wave than for the other U_ℓ thus necessit-
-ating virtually two different programs for the calculation of all the partial waves. To sum up it is perhaps sufficient to note that one calculation of the S wave contributions for the 1S2S excited states for the two-electron sequence reported by Winter and McKoy (W17) took no less than 1 hour of machine time on an IBM 360 - 75 whereas variational calculations using trial functions of the type (21) carried out by the author required only about 1/1000 of this, superior accuracy being obtained.

To retain the above advantages it is necessary that the variational trial functions be simple enough to give modest coding requirements yet still give the required accuracy. It was found that for all of the electron pair calculations reported in this work (14) or a simple variant of it fitted these criteria. For example for $\varepsilon 2(0)$ for the hydrogenic theory a 54 term function (large enough to give accuracy but kept to a reasonable size to avoid rounding problems) gave an energy of -0.125327 a.u. in exact agreement with the most accur-
-ate numerical calculation of Winter and McKoy (W17) and only marginally different from the variational results of Byron and Joachain (B19) and Knight and Scherr (K12) of -0.125334 and -0.125332 a.u. respect-
-ively.

For the numerical calculations a fourth difference approxi-
-mation of the derivatives (15) changing to only second differences at the boundaries was found to be most satisfactory.

$$f''(r_o) = \frac{1}{12} h^{-2} \left(-f(r_o+2h) + 16f(r_o+h) - 30f(r_o) + 16f(r_o-h) - f(r_o-2h)\right) \qquad (15)$$

The switch from one formula to another is due to the need at the boundaries when (15) is used to apparently know the value of the function outside of the region in which it is being determined. There are several means by which one can get round this difficulty of which the one noted above is the simplest. Over a series of trial calculations it was found that the use of more complicated formulae at the boundaries actually occasionally gave instability with no general enhancement in accuracy.

The region in which the U_{ℓ} have to be found ranges from 0 to ∞ in each dimension but for practical purposes a cutoff radius R_{max} has to be chosen for which it is assumed that $G_{\ell} = r_1 r_2 U_{\ell}$ vanishes.* This can be estimated for a series of calculations by carrying out a few trial computations with different values of R_{max} it being found for the problems described here that a boundary placed approximately where the value of the single-particle distribution function $P(r)$ falls to less than 10^{-4} usually gave a negligible truncation error. At the other boundaries G_{ℓ} is also taken to be zero.

The linear equations resulting on the finite-difference discretisation can, as previously stated, be conveniently solved using an iterative method. Successive OverRelaxation was employed although it was not found possible to determine any prescription for the optimum value of the relaxation parameter ω . However after a little exper--ience with these problems it proved feasible to estimate ω_{opt} such that substantially faster convergence than for the Gauss-Seidel ($\omega = 1$) technique could usually be achieved.

* Other boundary conditions have been suggested for example by Schulman and Lee (S5) but again the simplest choice seems to be generally the most useful.

Some final technical points which may be of interest are:-

1/ The use of a 'square root' grid (i.e. a transformation $r = x^2$) as described by Winter (W12) to give a more favourable distribution of points.

2/ Trapezoidal integration was employed for the evaluation of the $\mathcal{E}2(\ell)$ and for E3 as no advantage was discovered in the use of more complicated quadrature formulae.

3/ The primitive values of the third order energy could be smoothly extrapolated as for the components of E2 even although the S partial wave was not determined numerically.

C Results for the hydrogenic theories

In Table 2.1 are recorded the partial wave components of E2 using hydrogenic and screened hydrogenic perturbation theory with a value of σ of 5/16 in the latter case. The calculations were carried out as described in the previous section, the only point of note in this regard being the use of an extremely simple variational function for the S wave for the screened potential:- here with a 'CI' function the exponential factors were taken as $\alpha = \beta = 1.0$ whereas for the hydro--genic study a few calculations were executed to determine approxima--tely optimum exponents.

From the Table it may be noted that while the contributions from the S waves differ radically those from the other partial waves

Table 2.1 A comparison of the partial wave components of E2 for the ground state of the two-electron sequence using hydrogenic and screened hydrogenic ($\sigma = 5/16$) theory.

ℓ	Hydrogenic	Screened hydrogenic
0	-0.125327	-0.027664
1	-0.026497	-0.026496
2	-0.003906	-0.003906
3	-0.001077	-0.001078
4	-0.000406	-0.000406
5	-0.000184	-0.000185
6	-0.000095	-0.000096
7	-0.000054	-0.000054
8	-0.000032	-0.000033
9	-0.000020	-0.000021
$\geqslant 10$	-0.000052	-0.000053
Total for $\ell \geqslant 1$	-0.032324	-0.032326
Total E2	-0.157651	-0.059990

are essentially identical. This is indeed as it should be since if the equations (9) are examined for the two types of perturbation theory for $\ell > 0$ with suitable changes of scale they can be transformed one into another with however the $\varepsilon 2(\ell)$ remaining constant in the same manner as E2 is the same for the whole sequence in hydrogenic theory. As might thus be expected the values of E2 and E3 for the two schemes can easily be shown to be interlinked and in general Pan and King (P1) give the expressions (16) to (19) for screened hydrogenic systems.

$$E0(\sigma) = -(Z-\sigma)^2 \qquad (16)$$

$$E1(\sigma) = (Z-\sigma)(0.625 - 2\sigma) \qquad (17)$$

$$E2(\sigma) = E2(0) + \sigma(0.625 - \sigma) \qquad (18)$$

$$E\,n\,(\sigma) = (Z-\sigma)^{2-n} \sum_{\ell=3}^{n} \binom{n-3}{n-k} (-\sigma)^{n-k}\, E\,k\,(0) \qquad (19)$$

Such expressions are a useful check on the internal consistency of the computational approach and in Table 2.2, along with the values of E2 and E3 calculated using the two perturbations, are the accurate hydrogenic values of Knight and Scherr (K12) and 'theoretical' values for the screened theory from equations (18) and (19) (N.B. all the sums through E2 should be identical). It can be seen that unless extreme accuracy is required the present method appears satisfactory with an error of about 0.02 Kcals in the energy through E3 or more than two orders of magnitude better than 'chemical accuracy'. It would also

Table 2.2 A comparison of values of E2 and E3 for hydrogenic and screened hydrogenic perturbation schemes for the ground state of He.

Hydrogenic results	This work	Knight & Scherr[a]
E2	-0.157651	-0.157666
E3	0.004373	0.004349
Sum through E2	-2.907651	-2.907666
Sum through E3	-2.903278	-2.903317

Screened hydrogenic	This work	'Theoretical'[b]	'Theoretical'[c]
E2	-0.059990	-0.059996	-0.060011
E3	0.005102	0.005183	0.005154
Sum through E2	-2.907646	-2.907651	-2.907666
Sum through E3	-2.902544	-2.902469	-2.902515

[a] Reference (K12).

[b] Evaluated from own hydrogenic results.

[c] Evaluated from hydrogenic results of Knight & Scherr (K12).

seem that this residual error could be at least partly removed fairly straightforwardly as, assuming the veracity of the value of -0.125334 a.u. for the S wave energy due to Byron and Joachain (B19), the error in the $\ell = 0$ components in Table 2.1 represents 50% and 75% of the total error in E2 for the two cases respectively. Nevertheless for the remainder of the calculations presented here such further elaboration was not found necessary and for the most part the simplicity of the above scheme could be preserved intact.

2.3 Studies of excited states using hydrogenic theory

A Theory and methods of solution

For the ^1SnS excited states in hydrogenic perturbation theory the relevant equations for the partial wave components of the first order wavefunction can be written as a simple generalisation (20) of (9).

$$\left(-\tfrac{1}{2}\left(r_1^{-2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1}\right) + r_2^{-2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2}\right)\right)\right.$$

$$\left. + \tfrac{1}{2}\frac{\ell(\ell+1)}{} \left(r_1^{-2} + r_2^{-2}\right) - r_1^{-1} - r_2^{-1} - \varepsilon^o_{1s} - \varepsilon^o_{ns}\right) U_\ell(r_1, r_2)$$

$$= \left(E1\ \delta_{\ell o} - \frac{r_<^\ell}{r_>^{\ell+1}}\right) R(r_1, r_2) \qquad (20)$$

where $R(r_1,r_2)$ is $R_{1s}(r_1)\, R_{ns}(r_2) \pm R_{ns}(r_1)\, R_{1s}(r_2)$ corresponding to singlet and triplet states respectively.

For the partial waves having ℓ greater than zero the only changes from the ground state procedure were the choosing of more generous radial cutoffs and a transformation to a 'cube root' grid i.e. $r = x^3$ rather than the 'square root' distribution previously employed. As before 20(5)40 strips in each dimension were used.

For the variational calculations trial functions of the form (21) were used with exponents $\alpha = 1.0$ and $\beta = 1.0/n$ with expansion lengths of up to 65 terms (m,n take the values 0,1 through to 10,10).

$$\Phi(r_1,r_2) = (r_1^m r_2^n + r_1^n r_2^m)(\exp(-\alpha r_1 - \beta r_2) \pm \exp(-\alpha r_2 - \beta r_1)) \qquad (21)$$

Although the states under investigation are not the lowest of their symmetry it should be noted that no attempt was in general made to make any allowance for this in the S wave functions, the exception being 1S2S ^{1,3}S. For the latter for the triplet there is no problem as this is the lowest ^{3}S state while for the singlet the zeroth 1S1S ^{1}S function was included in the variational basis.

B Results for the excited S states

In Table 2.3 the partial wave components of E2 are given for the 1S2S states while in Table 2.4 E2 and E3 for 1S2S ^{1,3}S and 1S3S ^{1,3}S are compared with the most accurate numerical and variational calculations which are available. For the 1S2S states the agreement with the results of other workers is excellent especially for the triplet state, it being of note that the variational values were all found

Table 2.3 The values of the partial wave contributions to E2 for the 1S2S states of the two-electron sequence calculated within hydrogenic perturbation theory.

ℓ	$1S2S\ ^1S$	$1S2S\ ^3S$
0	-0.106618	-0.045320
1	-0.006497	-0.001910
2	-0.000929	-0.000146
3	-0.000254	-0.000024
4	-0.000095	-0.000006
5	-0.000043	-0.000002
6	-0.000022	-0.7×10^{-6}
7	-0.000012	-0.3×10^{-6}
8	-0.000007	-0.2×10^{-6}
9	-0.000005	-0.8×10^{-7}
$\geqslant 10$	-0.000012	-0.1×10^{-6}
Total E2	-0.114499	-0.047408

Table 2.4 A comparison of the present results for the $1S2S\,^{1,3}S$ and $1S3S\,^{1,3}S$ states of the two-electron sequence with those of other workers.

	$1S2S\,^1S$		$1S2S\,^3S$		$1S3S\,^1S$		$1S3S\,^3S$	
	E2	E3	E2	E3	E2	E3	E2	E3
This work	-0.114499	0.009150	-0.047408	-0.004872	-0.048844	-0.002369	-0.032316	-0.002326
Winter[a]	-0.114486	0.009251	-0.047406	-0.004876	-	-	-	-
Variational[b] (162 terms)	-0.114487	0.009224	-0.047409	-0.004873	-0.049061	-0.000944	-0.032313	-0.002106
Variational[b] (96 terms)	-	-	-	-	-0.047906	0.005345	-0.032158	-0.001159
Variational[c] (85 or 86 terms)	-	-	-0.047409	-0.004874	-	-	-0.032309 -0.031756	-0.002167 -0.002587
Variational[d]	-0.114476 -0.114509	0.009415	-0.047409	-0.004872	-	-	-	-

[a] All partial waves calculated by numerical means ..... reference (W12).

[b,c] Results of J. Midtdal & co-workers. For results b, no attempt was made to include zeroth functions of same symmetry in variational basis (A1). For c, for the $1S3S\,^3S$ state this was carried out (results for 37 term expansion of the wave function are given below 86 term results) (L10).

[d] From the work of Knight & Scherr (K12). Second value of E2 for the $1S2S\,^1S$ state is from the highly accurate calculation of Knight (K11).

using expansions of the first order wavefunction involving very large numbers of terms in interelectron co-ordinates.

For the other states the results are expected to be progr--essively less accurate as n increases due mainly to the neglect of any consideration of the states which are lower in energy but of the same symmetry. Despite this the present values for the energy coefficients are not all that different from those evaluated by Midtdal and co-workers (A1, L10) for the 1S3S states and it is interesting that these come into better agreement as the number of terms in the variational functions of Midtdal et al is increased. In addition Table 2.5 lists E2, E3 and the total energy for He for all the states examined and it may be seen that although these calculations are deficient when compared with the remarkable computations of Pekeris (P3, A2) they do yield quite reasonable values for the energies of the two-electron sequence. For example for the 1S5S results, those for which the accuracy is certainly least, the error for Ne^{8+} is 1 part in 50 000 and 1 part in 650 000 for the singlet and triplet states respectively.

The above calculations can perhaps best be regarded as pilot studies of some of the more highly excited states of the two-electron sequence on the results of which more sophisticated researches can be based. With this in mind it is interesting that the S wave contribution to E2 rapidly becomes dominant as can be seen from Table 2.5. This is scarcely unexpected but it is of importance when one considers the obviously slow variational convergence of the calculations of Midtdal et al referred to above. These workers employ an expansion in Hylleraas variables for the first order function and while it is certainly true that the inclusion of interelectron co-ordinates in the wavefunction gives great accuracy when a 'dynamical pair' is the subject of the

Table 2.5 Values of E2, E3 and total energies (for the case of He) for the 1SnS states of the two-electron sequence.

State	E2	E3	% radial[a]	Total energy	Exact energy (P3, A2)
$1s^2$	-0.157651	0.008626	79.6	-2.90328	-2.90372
$1s2s\,^1S$	-0.114499	0.009150	93.0	-2.14628	-2.14597
$1s2s\,^3S$	-0.047408	-0.004872	95.6	-2.17399	-2.17523
$1s3s\,^1S$	-0.048844	-0.002369	95.7	-2.06174	-2.06127
$1s3s\,^3S$	-0.032316	-0.002326	98.4	-2.06826	-2.06869
$1s4s\,^1S$	-0.027632	-0.002403	96.5	-2.03389	-2.03359
$1s4s\,^3S$	-0.021298	-0.001093	99.1	-2.03626	-2.03651
$1s5s\,^1S$	-0.017366	-0.003356	97.3	-2.02166	-2.02118
$1s5s\,^3S$	-0.014825	-0.001135	99.3	-2.02271	-2.02262

[a] Percentage of E2 given by S wave.

perturbation treatment for different types of electron pair other trial functions would perhaps be more efficient. (This is supported for example by the results of Byron and Joachain (B20) and Sims and Hagstrom (S19) for the Be atom). For the 1SnS states from this present work it would appear that it is much more important for $n>3$ to accurately represent the S type or radially correlated terms than to compute the angularly correlated components with great precision.*

C The convergence of the partial wave expansion

In Tables 2.1 and 2.5 contributions to E2 from the U_ℓ with $\ell \geqslant 10$ are included although so far no indication has been given in the text of how these quantities were estimated. Schwartz (S10) has demonstrated that for the hydrogenic ground state calculation the contribution of each partial wave to E2 should, in the limit of high ℓ, be proportional to ℓ^{-4} and he conjectured that for singlet states the convergence should in general be $\propto \ell^{-4}$ due to the singularity in the r_{12}^{-1} term giving the peakedness about the line $\mathbf{r}_1 = \mathbf{r}_2$. For triplet states the antisymmetry of the space wavefunction however gives a node along the above line and he suggested that the convergence in this case would be considerably faster, namely $\propto \ell^{-6}$. Although a little work on this subject has been carried out (B19) it does not seem to have been generally investigated and for this purpose the $\varepsilon 2(\ell)$ were computed

* Accad, Pekeris and Schiff (A2) have also experienced some difficulty in ensuring convergence when employing trial functions in Hylleraas variables for calculations on excited states of the two-electron sequence. They attribute this to an inflexible exponential factor in their wavefunction which however may be considered as allowing for radial correlation between shells.

up to as high ℓ as was practicable for the 1SnS states utilising 20(5)50 strips on a 'square root' or 'cube root' grid. In Figures 2.1 and 2.2 $\log(|\varepsilon 2(\ell)|)$ is plotted versus $\log(\ell)$ for the singlet and triplet states with the proposed asymptotic gradients and it can be seen that the suggested terminal behaviour is confirmed for the differ--ent pairs. For the ground state Schwartz gave an explicit formula for the $\varepsilon 2(\ell)$ which was later corrected by White (W9) to the expression (22).

$$\varepsilon 2(\ell) = - \frac{45(\ell + 0.5)^{-4}}{256} \left(1.0 - 1.25(\ell + 0.5)^{-2} + \ldots \right) \qquad (22)$$

In Table 2.6 the values of the $\varepsilon 2(\ell)$ for $\ell = 5$, 10, 15 and 20 calculated using (22) are compared with the numerical values and the accurate variational study of Byron and Joachain (B19). Overall the results are in harmony though for $\ell = 20$ the error in the numerical values is probably about 10%, this being due to the concentration of U_{20} about the line $r_1 = r_2$ such that most of the grid points used in the calculation are "wasted" with the function having a negligible amplitude over most of the square region.

It may finally be remarked that nothing appears to be known about the convergence of E3 with ℓ. Rather it is generally assumed that this is rapid and the contribution of say U_ℓ with $\ell > 9$ will be of little consequence. However a very limited study by the author on the 1S2S ^1S state suggests that the terminal convergence might be extremely slow and hence may in part explain the somewhat larger errors observed in the E3 than in the E2. For the most part though E3 is an order of mag--nitude or more smaller than the second order energy, the effect of

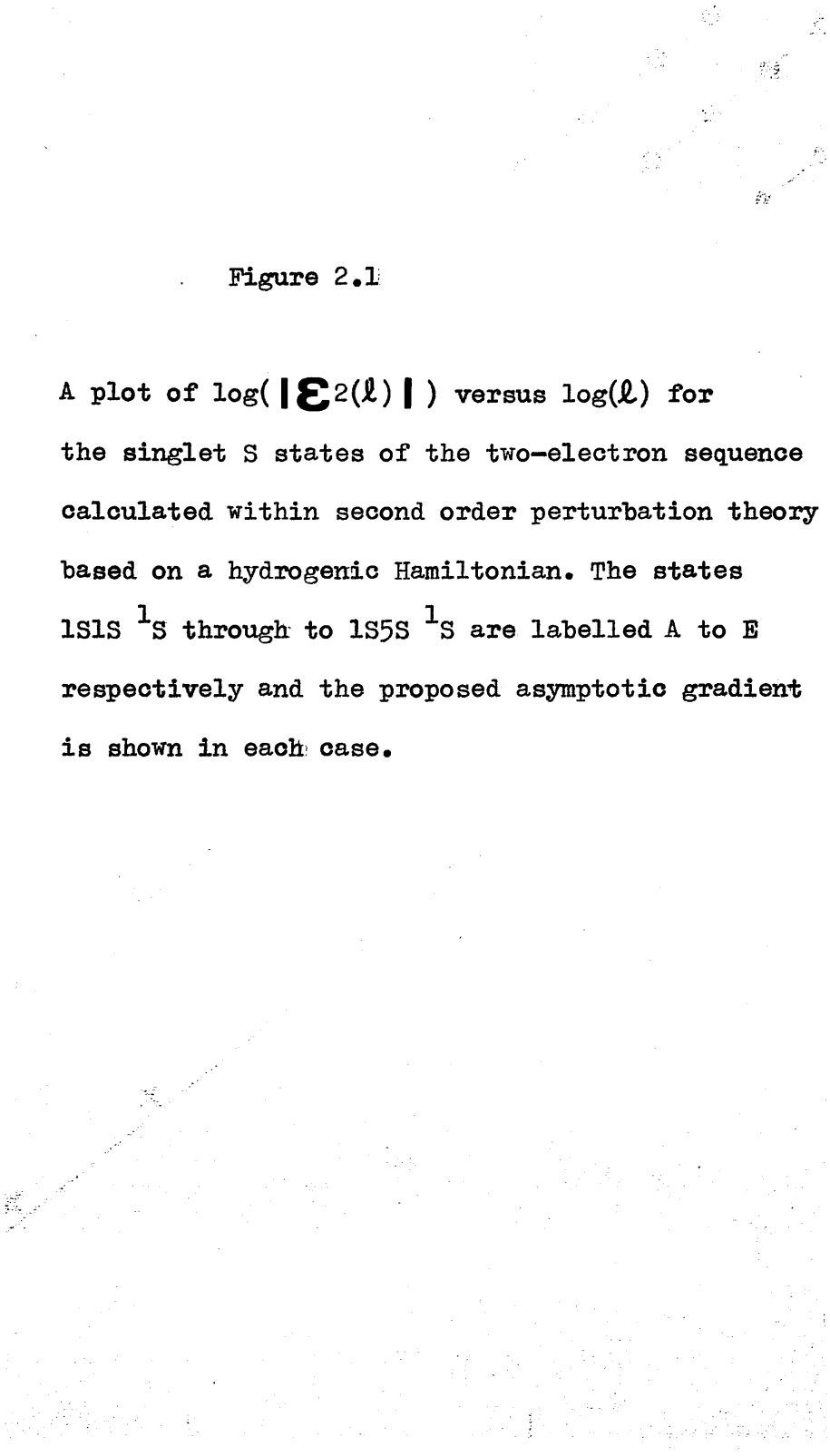


Figure 2.1

A plot of $\log(|\varepsilon^{2}(\ell)|)$ versus $\log(\ell)$ for the singlet S states of the two-electron sequence calculated within second order perturbation theory based on a hydrogenic Hamiltonian. The states $1S1S\ ^{1}S$ through to $1S5S\ ^{1}S$ are labelled A to E respectively and the proposed asymptotic gradient is shown in each case.

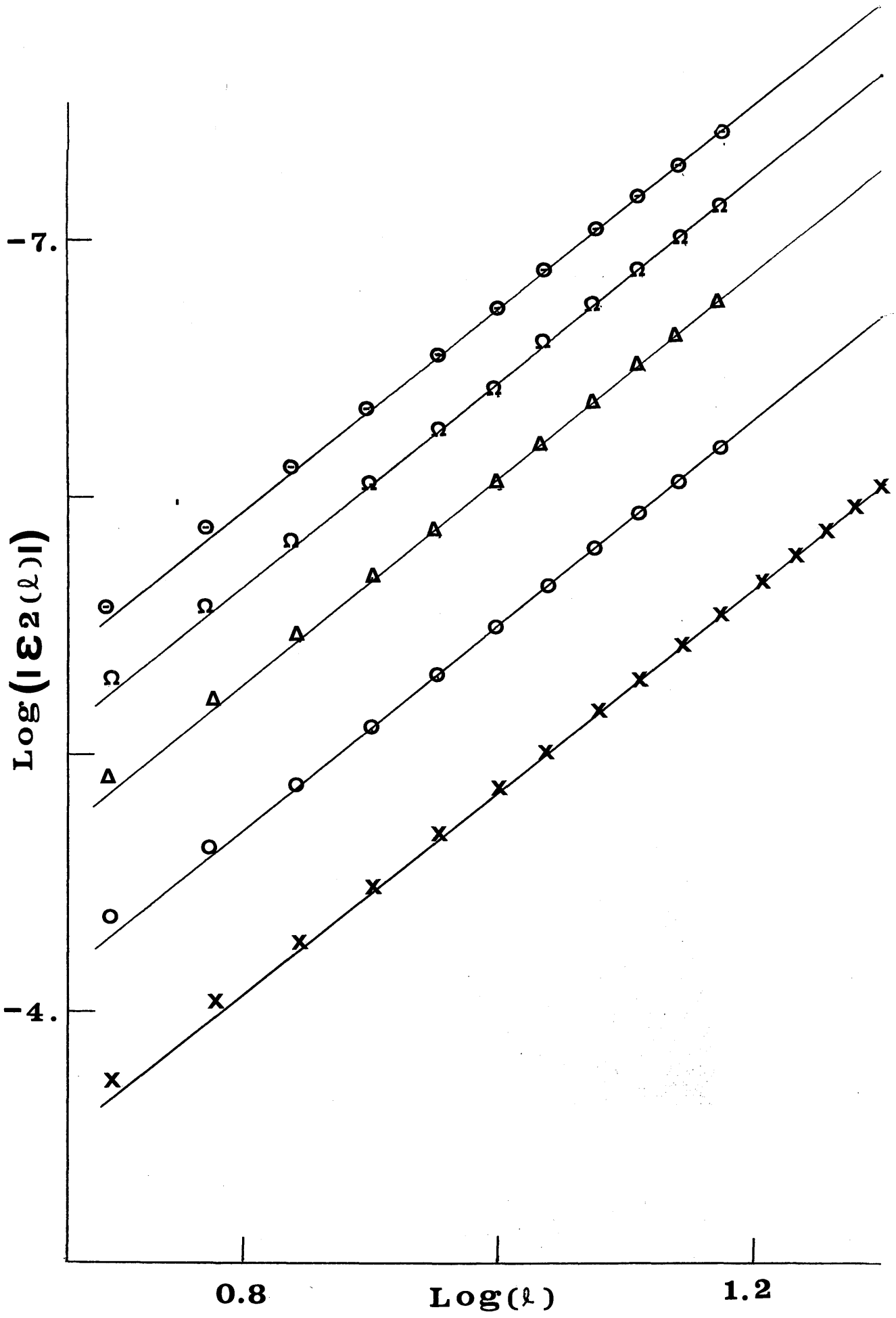

-7.
-4.
Log(|Ω2(ℓ)|)
0.8
Log(ℓ)
1.2

Figure 2.2

A plot of $\log(|\varepsilon_2(\ell)|)$ versus $\log(\ell)$ for the triplet S states of the two-electron sequence calculated within second order perturbation theory based on a hydrogenic Hamiltonian. The states $1S2S\ ^3S$ to $1S5S\ ^3S$ are labelled A to D respectively and the proposed asymptotic gradient is shown in each case.

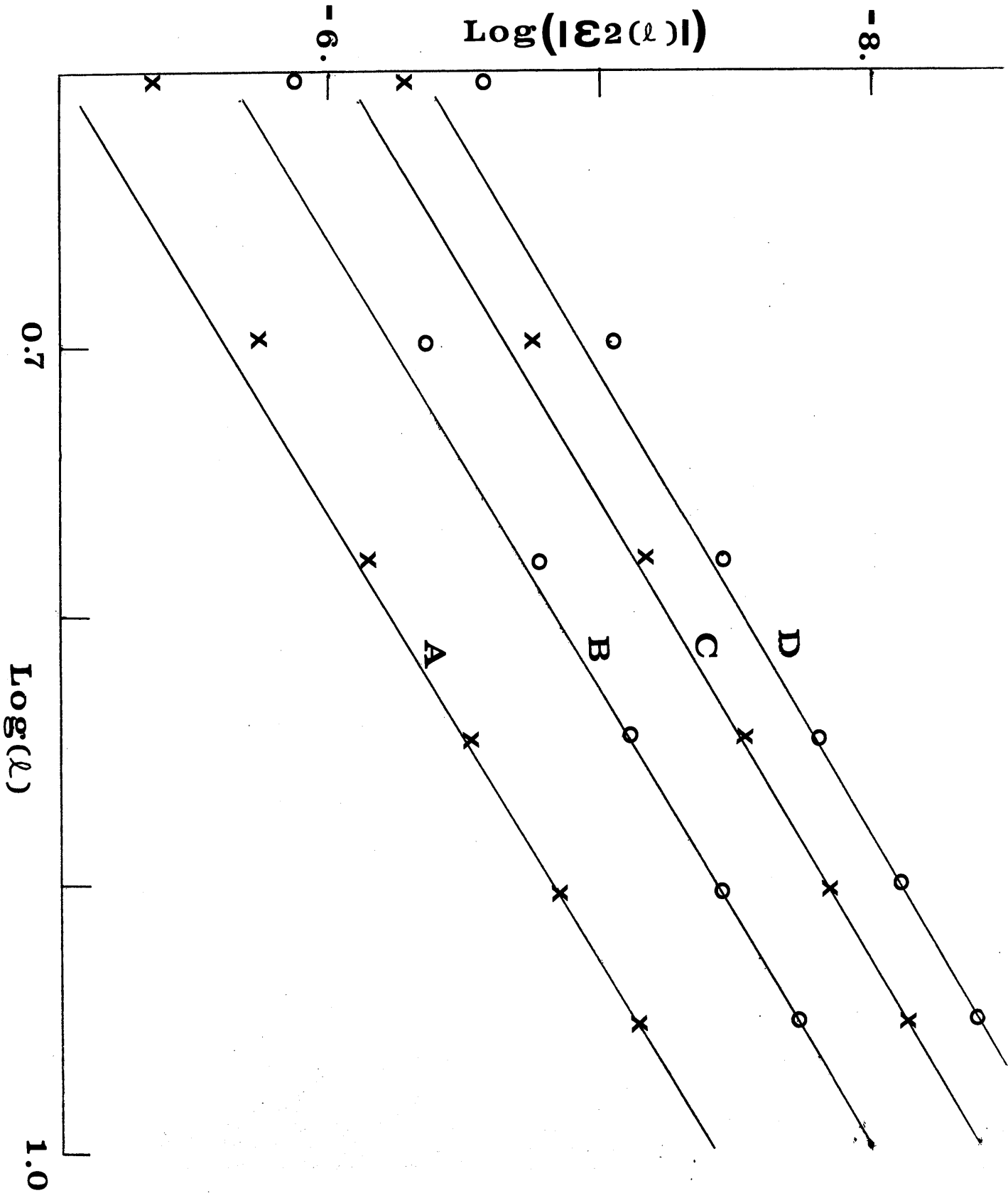

Log(|ε2(ℓ)|)
-.6
-.8
0.7
1.0
Log(ℓ)
A
B
C
D

Table 2.6 A comparison of values of some partial wave components of E2 for the ground state of the two-electron sequence based on hydrogenic perturbation theory. These are taken from the present work, the variational calculations of Byron and Joachain and the asymptotic formula as corrected by White.

l	Schwartz/White[a]	Byron & Joachain[b]	This work
5	-0.184×10^{-3}	-0.183×10^{-3}	-0.1850×10^{-3}
10	-0.143×10^{-4}	-0.138×10^{-4}	-0.1421×10^{-4}
15	-0.303×10^{-5}	—	-0.290×10^{-5}
20	-0.992×10^{-6}	-0.944×10^{-6}	-0.893×10^{-6}

[a] References (S10, W9).

[b] Reference (B19).

truncation being probably not too drastic though it is a topic which clearly requires investigation if it is desired to obtain very accurate values of the third order energy.

2.4 Ground state studies using a Hartree zeroth Hamiltonian

Most of 2.1 and 2.2 were concerned with the development of perturbation theory for two-electron atomic systems based on a hydrog--enic Hamiltonian. However for larger systems the complications involved in this scheme for example the complex form of the expression for the third order energy* make it worthwhile examining other possibilities. Hence in this section calculations based on a Hartree H^o, which may be thought of as the simplest form of the V^{N-1} potential frequently used in many-body perturbation theory (L5), will be considered for the ground state of the two-electron series from H^- through to Ne^{8+}.

Now for this choice of zeroth Hamiltonian ψ^o still is of the form (2) but the orbital satisfies the equation (23).**

$$(-\tfrac{1}{2}\nabla_1^2 - Z/r_1 + J(\mathbf{r}_1) - \varepsilon^o_{1s})\, \Phi_{1s} = 0 \qquad (23)$$

* See N.W.Winter, reference (W12) for the simple example of the Li isoelectronic sequence.

** N.B. for these systems the zeroth function is identical in Hartree and Hartree-Fock formalism but however the first and higher order corrections to the wavefunction differ entirely.

where

$$J(\mathbf{r}_1) = \int \Phi_{1s}(\mathbf{r}_2)\, r_{12}^{-1}\, \Phi_{1s}(\mathbf{r}_2)\, d\mathbf{T}_2 \qquad (24)$$

Expanding the first order pair function as before the equation (25) is obtained for each of the partial waves as has been shown by Winter, McKoy and Laferriere (W18).

$$\begin{aligned} &\left(-\tfrac{1}{2}\left(r_1^{-2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1}\right) + r_2^{-2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2}\right)\right)\right. \\ &\quad + \tfrac{1}{2}\ell(\ell+1)\,(r_1^{-2} + r_2^{-2}) - Z\,(r_1^{-1} + r_2^{-2}) + J(r_1) + J(r_2) \\ &\quad \left. -2\,\varepsilon_{1s}^{o}\right) U_\ell(r_1, r_2) \\ &= \left((E1 + J(r_1) + J(r_2))\,\delta_{\ell o} - \frac{r_<^\ell}{r_>^{\ell+1}}\right) R_{1s}(r_1)\, r_{1s}(r_2) \end{aligned} \qquad (25)$$

$$\text{with} \quad E1 = -\left\langle \Phi_{1s}\, \Phi_{1s} \,\middle|\, r_{12}^{-1} \,\middle|\, \Phi_{1s}\, \Phi_{1s} \right\rangle \qquad (26)$$

The second and third order energies are easily found and are given by (27) and (28).

$$\begin{aligned} E2 = \sum_\ell (2\ell+1)^{-1} \int & R_{1s}(r_1)\, r_{1s}(r_2) \\ & \times \left(\frac{r_<^\ell}{r_>^{\ell+1}} - \delta_{\ell o}\,(E1 + J(r_1) + J(r_2))\right) \\ & \times U_\ell(r_1, r_2)\, r_1^2\, r_2^2\, dr_1\, dr_2 \end{aligned} \qquad (27)$$

$$E3 = \sum_{\ell,\ell',k} C^k(\ell,\ell') \int U_\ell(r_1,r_2) \frac{r_<^k}{r_>^{k+1}} U_{\ell'}(r_1,r_2)\, r_1^2\, r_2^2\, dr_1\, dr_2$$

$$- \sum_{\ell} (2\ell+1)^{-1} \int U_\ell^2(r_1,r_2)\, (E1 + J(r_1) + J(r_2))$$

$$\times r_1^2\, r_2^2\, dr_1\, dr_2$$

$$- 2.0 \times E2 \int U_o(r_1,r_2)\, R_{1s}(r_1)\, R_{1s}(r_2)\, r_1^2\, r_2^2\, dr_1\, dr_2 \qquad (28)$$

where $C^k(\ell,\ell')$ still is defined as in (12).

It is apparent on examination of the above equations that they do not differ greatly from their counterparts for the hydrogenic formalism. Thus it would seem likely that similar methods of solution could be used to determine the U_ℓ :-

For the S waves a simple expansion of the type that was employed for the screened hydrogenic calculations was utilised with orbital exponents given the value Z. The other partial waves were found on a 'square root' grid with 20(5)40 strips in each dimension and appropriate radial cutoffs. For the zeroth functions those of Clementi (C7) were taken as the required basis with the exception of the hydride ion for which the corrected orbital of Curl and Coulson (C11) was utilised.

In Table 2.7 the partial wave components of E2, the total E2 and E3 are collected for a number of the systems investigated. The most striking difference in comparison with the hydrogenic calculations is, of course, the substantial reduction in the S wave contribution to the second order energy as one would expect as the Hartree function should be much more like the spherical component of the exact wave-

Table 2.7 Partial wave contributions to E2, total E2 and E3 for H^-, He, Be^{2+} and Ne^{8+} using Hartree perturbation theory.

ℓ	H^-	He
0	-0.02836	-0.01798
1	-0.02188	-0.02480
2	-0.00327	-0.00368
3	-0.00091	-0.00102
4	-0.00034	-0.00038
5	-0.00016	-0.00017
6	-0.00008	-0.00009
7	-0.00005	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant$10	-0.00004	-0.00005
Total E2	-0.05513	-0.04827
E3	0.02388	0.00733

ℓ	Be^{2+}	Ne^{8+}
0	-0.01579	-0.01487
1	-0.02575	-0.02622
2	-0.00381	-0.00387
3	-0.00105	-0.00107
4	-0.00040	-0.00040
5	-0.00018	-0.00018
6	-0.00009	-0.00009
7	-0.00005	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant$10	-0.00005	-0.00005
Total E2	-0.04722	-0.04686
E3	0.00322	0.00121

-function than the hydrogenic zeroth basis. The other components of E2 are not particularly unlike those arising in the hydrogenic theory especially as ℓ increases and it is apparent that as Z rises the Hartree $\varepsilon 2(\ell)$ are converging smoothly to the hydrogenic values from above.

In Table 2.8 are listed for He the results of the present work and those of a variety of other calculations on the same problem. The overall agreement between the different sets of computations is excellent but possibly a little fortuitous especially when it is considered that several different representations of the Hartree Φ_{1s} were used. Nevertheless comparison with what is probably the most accurate calculation, that of Riley and Dalgarno (R3), suggests that the error in E2 + E3 is unlikely to be more than a few hundred thousandths of a Hartree for the sequence. The possible errors in the total energies and the convergence of the perturbation series will be further discussed in 2.7.

2.5 Ground state studies using a Hartree-Fock H^o.

In the previous section some calculations for the two-electron sequence based on a Hartree H^o were described. However the zeroth function for that Hamiltonian is also an eigenfunction of the perhaps more familiar Hartree-Fock Hamiltonian with this time the orbital satisfying the equation (29).

$$(-\tfrac{1}{2}\nabla_1^2 - Z/r_1 + 2J(\mathbf{r}_1) - K(\mathbf{r}_1) - \varepsilon^o_{1s}) \Phi_{1s} = 0 \qquad (29)$$

Table 2.8 A comparison of results for He using Hartree perturbation theory through third order in the energy.

	S wave[a]	E2	E3	E2 + E3
This work	-0.01798	-0.04827	0.00733	-2.90262
Riley & Dalgarno[b]	---	-0.04830	0.00736	-2.90262
Winter et al[c] (W18)	-0.01802	-0.04825	0.00731	-2.90262
Byron & Joachain[d]	-0.01798	-0.04817 (-0.04804)	0.00717 (0.00713)	-2.90267 (-2.90258)
Weiss & Martin[e]	-0.01794	-0.04835	0.00741	-2.90262

[a] S wave contribution to E2.

[b] Variational calculation using trial function in Hylleraas variables, reference (R3).

[c] Finite-difference calculation with all partial waves found numerically.

[d] Variational trial functions for all partial waves (B19). Results in brackets were determined using a trial function in Hylleraas variables (B18).

[e] Reference (W8).

with

$$K(\mathbf{r}_1)\, f(\mathbf{r}_1) = \Phi_{1s}(\mathbf{r}_1) \int \Phi_{1s}(\mathbf{r}_3)\, r_{13}^{-1}\, f(\mathbf{r}_3)\, d\tau_3 \qquad (30)$$

The presence on the non-local operator $K(\mathbf{r})$ defined as in (30) this time yields an equation for the U_ℓ which is a good deal different from those already examined. The perturbation equation (31) furnishes the set of differential equations (32) containing integral terms in the U_ℓ in the inhomogeneity. Fortunately however they are still decoupled.

$$\begin{aligned}
&\left(-\tfrac{1}{2}\nabla_1^2 \; -\tfrac{1}{2}\nabla_2^2 - Z\,(r_1^{-1} + r_2^{-1}) + 2.0\ X\,(J(\mathbf{r}_1) + J(\mathbf{r}_2))\right. \\
&\left. - K(\mathbf{r}_1) - K(\mathbf{r}_2) - 2\varepsilon_{1s}^{\circ}\right)\psi^{I} \\
&= (E1 + 2.0\ X\,(J(\mathbf{r}_1) + J(\mathbf{r}_2)) - K(\mathbf{r}_1) - K(\mathbf{r}_2) - r_{12}^{-1})\,\psi^{\circ} \qquad (31)
\end{aligned}$$

$$\begin{aligned}
&\left(-\tfrac{1}{2}\left(r_1^{-2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + r_2^{-2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right)\right)\right. \\
&\left. + \tfrac{1}{2}\ell(\ell+1)\,(r_1^2 + r_2^2) - Z\,(r_1^{-1} + r_2^{-1}) - 2.0\ X\,(J(r_1) + J(r_2))\right. \\
&\left. - 2\,\varepsilon_{1s}^{\circ}\right)\, U_\ell(r_1, r_2) \\
&= \left((E1 + J(r_1) + J(r_2))\,\delta_{\ell o} - \frac{r_<^{\ell}}{r_>^{\ell+1}}\right) R_{1s}(r_1)\, R_{1s}(r_2) \\
&\quad + \frac{R_{1s}(r_1)}{(2\ell+1)} \int R_{1s}(r_3)\, \frac{r_{\min(1,3)}^{\ell}}{r_{\max(1,3)}^{\ell+1}}\, U_\ell(r_3, r_2)\, r_3^2\, dr_3 \\
&\quad + \frac{R_{1s}(r_2)}{(2\ell+1)} \int R_{1s}(r_3)\, \frac{r_{\min(2,3)}^{\ell}}{r_{\max(2,3)}^{\ell+1}}\, U_\ell(r_1, r_3)\, r_3^2\, dr_3 \qquad (32)
\end{aligned}$$

where

$$r_{min(x,y)} = min(r_x, r_y) \tag{33}$$

and

$$r_{max(x,y)} = max(r_x, r_y) \tag{34}$$

Once the partial waves have been found E2 and E3 can be determined from the expressions (27) and (35).*

$$E3 = \sum_{\ell,\ell',k} c^k(\ell,\ell') \int U_\ell(r_1,r_2) \frac{r_<^k}{r_>^{k+1}} U_{\ell'}(r_1,r_2)\, r_1^2\, r_2^2\, dr_1\, dr_2$$

$$- \sum_\ell (2\ell+1)^{-1} \int U_\ell^2(r_1,r_2)\, (E1 + 2.0 \times (J(r_1) + J(r_2)))$$

$$\times\, r_1^2\, r_2^2\, dr_1\, dr_2$$

$$- 2.0 \times E2 \int U_o(r_1,r_2)\, R_{1s}(r_1)\, R_{1s}(r_2)\, r_1^2\, r_2^2\, dr_1\, dr_2$$

$$+ \sum_\ell (2\ell+1)^{-2} \int U_\ell(r_1,r_2)\, ($$

$$R_{1s}(r_1) \int R_{1s}(r_3) \frac{r_{min(1,3)}^\ell}{r_{max(1,3)}^{\ell+1}} U_\ell(r_3,r_2)\, r_3^2\, dr_3 \; +$$

$$R_{1s}(r_2) \int R_{1s}(r_3) \frac{r_{min(2,3)}^\ell}{r_{max(2,3)}^{\ell+1}} U_\ell(r_1,r_3)\, r_3^2\, dr_3)\, r_1^2 r_2^2\, dr_1 dr_2 \tag{35}$$

* These expressions have been previously derived by Winter, McKoy and Laferriere (W18). However they are reproduced in full here as the statement in the literature appears to contain some typographical errors.

As before the S wave component of the first order function was determined variationally using a simple 'CI' type of trial function and, although the matrix elements are a little more complicated, the computational requirements and the resultant accuracy were found to be about the same as for the Hartree studies. For the other U_ℓ a strategy a little different from before was needed:- Owing to the integral terms the equations have to be solved iteratively by first finding the solution assuming the former to be zero and then evaluating the integrals and re-solving, the process being continued until the appropriate $\varepsilon 2(\ell)$ was constant to the desired accuracy. The result of this is to increase the processing time considerably, the time required to evaluate the integral terms alone being non-trivial. Certain factors however prevent this from becoming unreasonable e.g. the effect of the K(r) diminishes rapidly as ℓ increases and only a few complete cycles are required for the higher waves. It was also found that a judicious choice of relaxation parameters/numbers of cycles of relaxation can accelerate convergence considerably. Nevertheless it should not be concealed that the solution of an equation of the type (32) may require about 3 or 4 times the machine time required for the corresponding equation containing only local terms. For these calculations the details of numbers of grids, radial cutoffs, zeroth functions are the same as for the Hartree studies.

In Table 2.9 details of E2 and E3 are given for H^-, He, Be^{2+} and Ne^{8+} while in Table 2.10 a comparison is made with the work of others for He. Unfortunately data for this problem is much sparser than for the simpler Hartree calculation but again radically different methods appear to give results which are in harmony. As far as the behaviour of the $\varepsilon 2(\ell)$ is concerned the insensitivity to the particular field in the zeroth Hamiltonian (i.e. hydrogenic, Hartree, Hartree-Fock) as ℓ and Z increase is apparent. Before considering this point further

Table 2.9 Partial wave contributions to E2 for H^-, He, Be^{2+}, Ne^{8+} derived using Hartree-Fock perturbation theory.

ℓ	H^-	He
0	-0.01400	-0.01347
1	-0.01278	-0.01898
2	-0.00240	-0.00319
3	-0.00074	-0.00093
4	-0.00030	-0.00036
5	-0.00014	-0.00017
6	-0.00007	-0.00009
7	-0.00004	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant 10$	-0.00004	-0.00005
Total E2	-0.03057	-0.03734
E3	-0.00505	-0.00365

ℓ	Be^{2+}	Ne^{8+}
0	-0.01378	-0.01410
1	-0.02253	-0.02484
2	-0.00356	-0.00377
3	-0.00101	-0.00105
4	-0.00039	-0.00040
5	-0.00018	-0.00018
6	-0.00009	-0.00009
7	-0.00005	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant 10$	-0.00005	-0.00005
Total E2	-0.04169	-0.04459
E3	-0.00225	-0.00103

Table 2.10 A comparison of results for the ground state of He using Hartree-Fock perturbation theory through third order in the energy.

	S wave[a]	E2	E3	E2 + E3
This work	-0.01347	-0.03734	-0.00365	-2.90267
Byron & Joachain[b]	-0.01347	-0.03725	-0.00377	-2.90269
Byron & Joachain[c]	—	-0.03719	-0.00346	-2.90232
Winter et al[d]	-0.01350	-0.03731	-0.00367	-2.90266

[a] S wave contribution to E2.

[b] Legendre expansion of the wavefunction. All partial waves calculated variationally (B19).

[c] Expansion of the first order function in Hylleraas variables (B18).

[d] All partial waves determined numerically (W18).

a description of the final form of perturbation scheme examined will be given.

2.6 Perturbation studies based on the S limit wavefunction

A key point in the reduction of the first order pertur-bation equation to the set of decoupled elliptic equations is the expression of the electron interaction term in the series (36).

$$r_{12}^{-1} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\Theta_{12}) \qquad (36)$$

Instead of following a perturbation treatment the ground state space wavefunction can be similarly expressed and it is required to determine the U_l as before.

$$\Phi = \sum_{l=0}^{\infty} (4\pi)^{-1} (2l+1)^{\frac{1}{2}} U_l(r_1, r_2) P_l(\cos\Theta_{12}) \qquad (37)$$

Insertion of the wavefunction (37) into the Schrödinger equation leads to an infinite set of coupled equations for the partial waves and cont-aining the unknown eigenvalue E. It is of course not possible to solve such a set of equations but if the wavefunction is truncated after a few terms, say 5, the results might be expected to be fairly close to the exact solution. This indeed is the case as the results of Winter, Laferriere and McKoy (W15) have shown, but however the development of

the CI* rapidly becomes very complex as higher ℓ components are added. An interesting possibility would perhaps be to combine limited CI with perturbation theory, the latter being utilised to account for the higher order terms in the expression for r_{12}^{-1}. To this end the H^o (38) is used with the perturbation (39) which is r_{12}^{-1} less its spherical component.

$$H^o = -\tfrac{1}{2}\nabla_1^2 \; -\tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + r_>^{-1} \qquad (38)$$

$$H' = r_{12}^{-1} - r_>^{-1} = \sum_{\ell=1}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_\ell(\cos\Theta_{12}) \qquad (39)$$

Expansion of the perturbed wavefunction in Legendre form yields the equations (40) for the U_ℓ, here ℓ being greater or equal to one.

$$\begin{aligned} &\left(-\tfrac{1}{2}\left(r_1^{-2} \frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1}\right) + r_2^{-2} \frac{\partial}{\partial r_2}\left(r_2^2 \frac{\partial}{\partial r_2}\right)\right)\right. \\ &\left. +\tfrac{1}{2}\ell(\ell+1)\left(r_1^{-2} + r_2^{-2}\right) - Z\left(r_1^{-1} + r_2^{-1}\right) + r_>^{-1} - E^o\right) U_\ell(r_1, r_2) \\ &= -\frac{r_<^{\ell}}{r_>^{\ell+1}} R^o(r_1, r_2) \end{aligned} \qquad (40)$$

The forms for E2 and E3 are entirely analogous to those for the hydrogenic scheme with the only difference being the lack of an S component in Ψ'.

* The solution of the coupled set of equations is entirely equivalent to conventional Configuration Interaction ..... see also Chapter 9.

For the systems H^-, He, Li^+, B^{3+}, Ne^{8+} the equations were solved in the manner previously described using as zeroth functions the best S limit SOC functions of Davis (D9) which were assumed to be exact, and in Table 2.11 $\varepsilon 2(\ell)$, E2 and E3 are displayed for three calculations. Apart from the lack of $\ell = 0$ components the results rather resemble those from the Hartree calculations with the notable exception of H^-. However the latter is readily understandable when one observes the exceptionally high proportion (66.5%) of E_{corr} arising from radial correlation. With this in mind the good approximation which the sum through E3 affords to the exact energy for this system is not surprising.* In Table 2.12 the sums through first to third order in the energy are given along with the exact energies (P3) for the systems and also some results of calcul--ations of White, Ramaker and Schrader (W10). These authors base their perturbation on a wavefunction (41) which contains some, but not all, radial correlation and it is of interest that although E0 + E1 can differ quite considerably for the two schemes the other sums agree closely.

$$\psi^o = \exp(-\alpha r_> - \beta r_<) \qquad (41)$$

Finally it might be thought that the extension to higher orders for this form of perturbation theory would be straightforward

* It might be objected that both the relative and absolute errors in the energy are greater for H^- than for the other members of the sequence. However, as will be seen, all of the types of perturbation theory give a slowly convergent series for this ion and the results in question are actually comparatively good.

Table 2.11 Components of E2, total E2 and E3 for H^-, He and Ne^{8+} using perturbation theory based on the S limit wavefunction.

l	H^-	He	Ne^{8+}
0	0.00000	0.00000	0.00000
1	-0.01210	-0.02238	-0.02585
2	-0.00177	-0.00330	-0.00381
3	-0.00049	-0.00091	-0.00105
4	-0.00018	-0.00034	-0.00040
5	-0.00008	-0.00016	-0.00018
6	-0.00004	-0.00008	-0.00009
7	-0.00002	-0.00005	-0.00005
8	-0.00001	-0.00003	-0.00003
9	-0.00001	-0.00002	-0.00002
$\geqslant 10$	-0.00002	-0.00004	-0.00005
Total E2	-0.01474	-0.02731	-0.03154
E3	0.00374	0.00308	0.00064

Table 2.12 A comparison of the results using the S limit zeroth function and those of White, Ramaker and Schrader (W10).

	Z = 1	Z = 2	Z = 3
S limit			
E0 + E1[a]	-0.51449	-2.87902	-7.25249
E0 + E1 + E2	-0.52923	-2.90634	-7.28182
E0 + E1 + E2 + E3	-0.52549	-2.90326	-7.27971
White et al			
E0 + E1[a]	-0.50647	-2.87273	-7.24646
E0 + E1 + E2	-0.52851	-2.90635	-7.28184
E0 + E1 + E2 + E3	-0.52585	-2.90331	-7.27973
Exact (P3)	-0.52775	-2.90372	-7.27991

[a] For both schemes E1 is zero.

with no problems over the S components of the perturbed function. However it is easy to see that in fact for higher orders than first the nth order function will contain a spherical portion, the analogue in this type of perturbation theory of the 'radial adjustment' process in CI as angular terms are added to the wavefunction (D8).

2.7 Ground state energies for the sequence and the convergence of the perturbation schemes.

With regard to the calculations described in this Chapter two questions are apposite: Is perturbation theory through low order an appropriate method for calculating correlation energies in this isoelectronic sequence ? If so which scheme gives the most satisfactory results ?

A partial answer is immediately given to the first question from Table 2.13 where total energies for Z = 1.0 to 10.0 calculated from the various schemes are listed. It can be seen that apart from some of the results for the hydride ion the sums through E3 agree with the exact non-relativistic energies within 'chemical accuracy' (about 3 Kcals or 0.005 a.u.) with even in the worst case an error of no more than 0.008 a.u.. The values of the correlation energies provided by these computa--tions are thus fairly satisfactory with for example for the Hartree-Fock studies for H^-, He and Ne^{8+} an estimated 89.6, 97.5 and 99.8 % of E_{corr} being recovered. Even though there is some bias towards the more highly ionised species this is not large enough to seriously distort the behaviour of the correlation energy as a function of atomic number viz.

Table 2.13 A comparison of values of the total energy for the two electron sequence ground state employing the perturbation schemes described here through third order in the energy.

Z	Hydrogenic	Screened hydrogenic	Hartree	Hartree-Fock	S limit	Exact (P3)
1.0	-0.52392	-0.52012	-0.5193	-0.5236	-0.52549	-0.52775
2.0	-2.90328	-2.90254	-2.90262	-2.90267	-2.90326	-2.90372
3.0	-7.27974	-7.27944	-7.27946	-2.27939	-7.27971	-7.27991
4.0	-13.65547	-13.65531	-13.65526	-13.65520	-	-13.65557
5.0	-22.03090	-22.03081	-22.03075	-22.03070	-22.03095	-22.03097
6.0	-32.40619	-32.40613	-32.40607	-32.40603	-	-32.40625
7.0	-44.78140	-44.78136	-44.78130	-44.78127	-	-44.78145
8.0	-59.15656	-59.15653	-59.15647	-59.15644	-	-59.15660
9.0	-75.53168	-75.53166	-75.53161	-75.53159	-	-75.53171
10.0	-93.90678	-93.90676	-93.90676	-93.90672	-93.90677	-93.90681

All results are subject to some uncertainty in the last decimal place. For the last three schemes deficiencies in E0 and E1 are probably as important as those in E2 and E3 e.g. for the S limit result for $Ne.^{8+}$

a monotonic approach of the correlation energy from above to an asymptotic value of about -0.046 a.u. as $Z \longrightarrow \infty$.

The present work is however only of value if it is competi--tive with other procedures for the determination of the correlation energy for these and other atomic systems. Two methods are commonly used for this purpose:- The first is the inclusion of interelectron co-ord--inates in a variational approximation of the exact wavefunction, this being undoubtedly superior to any other method if refined to the degree associated with the work of Pekeris (P3). Such calculations are though extremely lengthy and complex and despite some extension to larger atoms for example by Gentner and Burke (G2) it is difficult to believe that the calculation of atomic structures in many-electron systems will be generally feasible in the near future.

The other, and more generally employed, method is CI. In Table 2.14 for a number of members of the He sequence HF perturbation results are compared with the CI calculations of Weiss[1] (W6) from which it obvious that CI has a marked advantage only for H^- where radial correlation is dominant. Otherwise as the 'dynamical' character of this type of pair becomes more marked as Z increases perturbation methods appear to account much more satisfactorily for the intricate correlation effects which give rise to (d,d'), (f,f') ..... excitations in CI. As will be seen later for other atomic systems low order perturbation theory appears to yield adequate results for correlation energies apart from cases where an analogous CI calculation is dominated by one or two

[1] For some of these systems better CI results have since been calculated by other workers. It was felt however to be more desirable to have a consistent group of calculations rather than a mixture of studies of differing accuracy.

Table 2.14 A comparison of the CI results of Weiss (W6) with the present Hartree-Fock perturbation theory for the two electron sequence.

	Z = 1		Z = 2		Z = 3		Z = 8	
	E	Δ%[a]	E	Δ%	E	Δ%	E	Δ%
S[b]	-0.51439	66.5	-2.87896	41.2	-7.25242	36.8	-59.12595	32.7
P	-0.52647	30.4	-2.90039	51.0	-7.27575	53.6	-59.15130	55.8
D	-0.52730	2.1	-2.90258	5.2	-7.27845	6.2	-59.15467	7.4
F	-0.52747	0.4	-2.90307	1.2	-7.27908	1.4	-59.15549	1.8
G	-0.52751	0.1	-2.90320	0.3	-7.27924	0.4	-59.15570	0.5
Perturbation theory	-0.5236	89.6	-2.90267	97.5	-7.27939	98.8	-59.15644	99.6
Exact	-0.52775	100.0	-2.90372	100.0	-7.27991	100.0	-59.15660	100.0

[a] Percentage of correlation energy added at each stage of calculation

[b] S, P etc. limit CI functions

types of **configuration**.* With reference to these remarks and those of section 2.3 B it is notable that the S limit energy for the 1S2S ^3S state of He is appreciably deeper at -2.17427 a.u. than the hydrogenic perturbation theory sum through E3 at -2.17399 a.u., the exact non-rela--tivistic energy being -2.17523 a.u. (D8, P3). Thus finally it may be speculated that electron pair correlation energies can be computed acc--urately by the use of CI or low order perturbation theory, one method being suitable when the other is only slowly convergent.

The second question which was asked concerned the relative rates of convergence of the different schemes. This subject has been extensively researched in the past yet even here there are one or two surprises. From Table 2.14 the well-known superiority of the hydrogenic perturbation theory is apparent and also the lack of improvement when a positive screening factor is employed (M11, P1). In addition it is obvi--ous that for highly ionised species convergence is rapid and its rate is about the same for all approaches, a feature which is brought out in Table 2.15 where E2, E3 and % $|E3/E2|$ are listed for the Hartree, Hartree-Fock and S limit schemes. Lastly as previously noted the S limit method furnishes a high proportion of the correlation energy, this being entirely reasonable as radial correlation is accounted for in the zeroth function. However while all of the above facts are already known or might reasonably be suspected it is not a little unexpected that the low order Hartree-Fock perturbation theory gives such a good total energy

* It seems quite likely that the same could be said for a comparison of results from CI and from wavefunctions containing Hylleraas variables e.g. see 2.3 B. However this is largely conjecture at present without further evidence on this point.

Table 2.15 Values of E2 and E3 for the isoelectronic sequence H^- - Ne^{8+} using Hartree, Hartree-Fock and S limit zeroth Hamiltonians.

	Hartree			Hartree-Fock			S Limit		
Z	E2	E3	%|E3/E2|	E2	E3	%|E3/E2|	E2	E3	%|E3/E2|
1.0	-0.05513	0.02388	43.3	-0.03057	-0.00505	16.5	-0.01474	0.00374	25.4
2.0	-0.04827	0.00733	15.2	-0.03734	-0.00365	9.8	-0.02731	0.00308	11.3
3.0	-0.04750	0.00446	9.4	-0.04018	-0.00280	7.0	-0.02934	0.00212	7.2
4.0	-0.04722	0.00322	6.8	-0.04169	-0.00225	5.4	-	-	-
5.0	-0.04707	0.00251	5.3	-0.04263	-0.00188	4.4	-0.03072	0.00128	4.2
6.0	-0.04698	0.00206	4.4	-0.04326	-0.00161	3.7	-	-	-
7.0	-0.04692	0.00175	3.7	-0.04372	-0.00141	3.2	-	-	-
8.0	-0.04687	0.00152	3.2	-0.04406	-0.00126,	2.9	-	-	-
9.0	-0.04684	0.00134	2.9	-0.04435	-0.00113	2.6	-	-	-
10.0	-0.04686	0.00121	2.6	-0.04459	-0.00103	2.3	-0.03154	0.00064	2.0

for the hydride ion.* It is difficult to rationalise this result though the better convergence of the HF series, at least to this low order, compared with that for the Hartree scheme is apparent from Table 2.15. Overall too it is difficult to see how one could judge a priori which type of scheme to apply to a particular system so as to compute the maximum percentage of the correlation energy with minimum effort. Evidently even straightforward perturbation calculations on such simple systems cannot be said to be at all properly understood.

2.8 Conclusions

In this Chapter it has been seen that numerical methods can be used to advantage in studies of electron correlation in two-electron atomic systems with an eclectic approach being adopted with the blending of numerical techniques with more conventional variational methods. To some extent this is aesthetically displeasing yet it is apparent that this mixture of computational techniques is both efficient and accurate for this type of calculation, the programming requirements especially being not excessive. It should though be recognised that for any specific investigation it may be more satisfactory to employ purely a numerical or a variational approach but this certainly does not invalidate the

* There is no doubt about the validity of this result. The difference between the sums through E3 for the Hartree and HF perturbation methods is more than an order of magnitude greater than the expected errors in these quantities, the Hartree result being in excellent agreement with the results of Weiss and Martin (W8) for this problem.

above conclusions.* Rather the scope for the accurate calculation of atomic wavefunctions is greatly enhanced by the possibility of using one or a combination of these powerful weapons.

An important aspect of the present work is simplicity. The latter will be a recurrent theme throughout this thesis as it is attemp--ted to demonstrate that the use of very simple computational techniques can render many quantities of physical interest accessible to practical calculation. The development of this subject will be continued in the next Chapter in which the calculation of correlation energies in many-electron atoms, notably the beryllium isoelectronic sequence, will be discussed.

****

* The first order calculation of 1S2P pairs in the two-electron sequence is an obvious example of this. Here the equations for the U_l are not decoupled and it would be awkward to use a combination of methods as in the bulk of this Chapter.

Chapter 3 Pair Correlation Energies in Many-Electron Atoms.

3.1 Introduction

Since the pioneering effort of Sinanoglu (S20) in the early nineteen-sixties a vast amount of effort has been exerted in the calculation of correlation energies in small atoms and molecules using the electron pair approach. Broadly in this type of method it is assumed that the correlation energy for the system in question can be partitioned as a sum of correlation energies for the different electron pairs const--ituting it. Clearly the great advantage of such an approximation is that it allows the correlation energy to be calculated one part at a time hence keeping the problem within manageable bounds. This is not the case for an all-electron calculation and for example the number of configurations required in CI to give say 80 - 90 % of the correlation energy can rapidly reach astronomical proportions. No attempt will be made here to generally justify the pair model or review the various schemes which have been proposed within this overall approach, an excellent exposition on this subject having been given in the recent book by Schaefer (S2). It is enough to say that for a large number of systems it would seem a sufficiently good approximation to obtain the correlation energy to chemical accuracy, provided of course that the pair correlation energies can be evaluated. In this Chapter it is intended to show that the numerical methods developed earlier in this work can greatly assist in this task.

As noted above several approaches have been suggested within the ambit of the pair method. Here Hartree-Fock perturbation theory through first order in the wavefunction as detailed by Byron and Joachain

in reference (B20) will be employed. Many cogent arguments can be advan--ced for such a choice, possibly the most powerful being that such an alternative leads to an intuitively appealing model in which the calcul--ated correlation energy is the sum of pair contributions, interpair effects being negligible to the order of perturbation theory considered. With regard to the last point, since the energy is summed through E3, the computed correlation energy cannot appreciably overshoot the true value of this quantity as can occur for example in Nesbet's version of the Bethe-Goldstone scheme (N3, V3, S2).

The bulk of this Chapter will be concerned with calculations on the Be isoelectronic sequence, this being a full report on some previously published work (W3), but some preliminary calculations on the Ne series will also be briefly discussed. In the first few sections the relevant pair equations will be derived and the numerical and variational techniques used to solve them elucidated. The different electron pair correlation energies will then be examined with special emphasis on their behaviour as a function of atomic number and also total energies will be given with it is hoped some illumination of the problem of the electron affinity of Li. Finally future work on other atomic systems notably the Ne isoelectronic sequence will be outlined.

3.2 Derivation of the pair equations for the Be isoelectronic sequence.

In this section the first order pair equations in HF perturbation theory will be derived following the approach of Byron and Joachain (B20) for the ground state of the beryllium isoelectronic sequence. As an extensive account of this has already been given by these

authors only sufficient to ensure lucidity will be included.

For the system in question a zeroth Hamiltonian of the form (1) is taken with the eigenfunction (4).

$$H^{o} = \sum_{j=1}^{4} h^{o}(j) \tag{1}$$

where

$$h^{o}(j) = -\tfrac{1}{2}\nabla_j^2 - Z/r_j + \sum_{i=1}^{4} V_i(\mathbf{r}_j) \tag{2}$$

and

$$V_i(\mathbf{r}_1) = \left\langle \chi_i \left| r_{12}^{-1} (1 - P_{12}) \right| \chi_i \right\rangle \tag{3}$$

$$\Psi^{o} = A \left(\prod_{j=1}^{4} \chi_j \right) \tag{4}$$

Now for Be there are four spin orbitals $\chi_{1s\uparrow}$, $\chi_{1s\downarrow}$, $\chi_{2s\uparrow}$, $\chi_{2s\downarrow}$ which are factored into space and spin parts as in (5), with the space part being a solution of a single-particle equation such as (6).

$$\chi_{1s\uparrow} = \phi_{1s}\alpha; \qquad \chi_{1s\downarrow} = \phi_{1s}\beta \tag{5}$$

$$\left(-\tfrac{1}{2}\nabla_1^2 - Z/r_1 + V_{1s}^{d}(\mathbf{r}_1) + 2\,V_{2s}^{d}(\mathbf{r}_1) - V_{2s}^{e}(\mathbf{r}_1) - \varepsilon_{1s}^{o} \right) \phi_{1s}(\mathbf{r}_1) = 0 \tag{6}$$

where

$$V^{d}_{ns}(\mathbf{r}_1) = \int \phi_{ns}(\mathbf{r}_2)\, r_{12}^{-1}\, \phi_{ns}(\mathbf{r}_2)\, d\tau_2 \qquad (7)$$

and

$$V^{e}_{ns}(\mathbf{r}_1)\, f(\mathbf{r}_1) = \phi_{ns}(\mathbf{r}_1) \int \phi_{ns}(\mathbf{r}_2)\, r_{12}^{-1}\, f(\mathbf{r}_2)\, d\tau_2 \qquad (8)$$

Now the RHF energy is given by E0 + E1, these quantities being defined as :-

$$E0 = 2\,\varepsilon^{o}_{1s} + 2\,\varepsilon^{o}_{2s} \qquad (9)$$

$$E1 = \langle \Psi^{o} | H' | \Psi^{o} \rangle = -V_{1s1s} - V_{2s2s} - 4\,V_{1s2s} + 2\,V_{ex} \qquad (10)$$

in the notation of Byron and Joachain.

The H' in (10) is defined as in (11) i.e. the difference between the true electron interaction terms and the sum of the Hartree-Fock single-particle potentials.

$$H' = \sum_{i<j} r_{ij}^{-1} - \bar{V}(\mathbf{r}_1) - \bar{V}(\mathbf{r}_2) - \bar{V}(\mathbf{r}_3) - \bar{V}(\mathbf{r}_4) \qquad (11)$$

with

$$\bar{V}(\mathbf{r}_i) = \sum_{j=1}^{4} V_j(\mathbf{r}_i) \qquad (12)$$

If a solution of the first order perturbation equation (13) can now be found then it would seem reasonable that the energy sums through E2 and E3 would account for a substantial part of the correlation energy, E2 and E3 being given by the expressions (14) and (15).

$$(H^{\circ} - E0)\,\Psi' = (E1 - H')\,\Psi^{\circ} \qquad (13)$$

$$E2 = \langle \Psi^{\circ} | H' - E1 | \Psi' \rangle \qquad (14)$$

$$E3 = \langle \Psi' | H' - E1 | \Psi' \rangle - 2\,E2 \langle \Psi^{\circ} | \Psi' \rangle \qquad (15)$$

At first it would seem a hopeless task to try to find a solution to (13) owing to the number of electrons involved but however it is possible to reduce the problem at this order of perturbation theory to a solution of a series of two-electron calculations of the type dealt with in Chapter 2. Again following Byron and Joachain the first order function is taken to be of the form (16):-

$$\begin{aligned}\Psi'(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \mathbf{S}\,(&F'_{k\ell}(\mathbf{r}_1, \mathbf{r}_2)\,\chi_m(\mathbf{r}_3)\,\chi_n(\mathbf{r}_4) + \\ &F'_{km}(\mathbf{r}_1, \mathbf{r}_3)\,\chi_\ell(\mathbf{r}_2)\,\chi_n(\mathbf{r}_4) + F'_{kn}(\mathbf{r}_1, \mathbf{r}_4)\,\chi_\ell(\mathbf{r}_2)\,\chi_m(\mathbf{r}_3) + \\ &F'_{\ell m}(\mathbf{r}_2, \mathbf{r}_3)\,\chi_k(\mathbf{r}_1)\,\chi_n(\mathbf{r}_4) + F'_{\ell n}(\mathbf{r}_2, \mathbf{r}_4)\,\chi_k(\mathbf{r}_1)\,\chi_m(\mathbf{r}_3) + \\ &F'_{mn}(\mathbf{r}_3, \mathbf{r}_4)\,\chi_k(\mathbf{r}_1)\,\chi_\ell(\mathbf{r}_2))\end{aligned} \qquad (16)$$

where k, ℓ, m, n, denote $1s\uparrow$, $1s\downarrow$, $2s\uparrow$, $2s\downarrow$.

In the expression for the first order function $\mathbf{S}$ permutates the $\mathbf{r}_i$ symmetrically and introduces the appropriate normalisation factor. The F^1_{ij} are antisymmetric two-particle functions and hence the total wavefunction through first order is antisymmetric.

It can be shown that there is no loss of generality in taking the F^1_{ij} to be orthogonal to all occupied orbitals as in (17).

$$\left\langle F^1_{ij}(\mathbf{r}_1, \mathbf{r}_2) \,|\, \chi_k(\mathbf{r}_1) \right\rangle = \left\langle F^1_{ij}(\mathbf{r}_1, \mathbf{r}_2) \,|\, \chi_k(\mathbf{r}_2) \right\rangle = 0 \qquad (17)$$

Thus the intuitive attractiveness of the scheme becomes apparent: Ψ' is seen as being added to Ψ° to allow for the correlation of each elec-tron pair while the other electrons remain in unperturbed orbitals.

Now proceeding from the functional (18) with the first order function (16) decoupled equations for each of the F^1_{ij} are found, these being entirely analogous to those already dealt with for two-electron atoms.

$$\mathbf{F} = \left\langle \Psi'_t | H^\circ - E0 | \Psi'_t \right\rangle + 2 \left\langle \Psi'_t | H' - E1 | \Psi^\circ \right\rangle \qquad (18)$$

$$(h^\circ(1) + h^\circ(2) - \varepsilon^\circ_i - \varepsilon^\circ_j) F^1_{ij}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= (\varepsilon^1_{ij} + V_i(\mathbf{r}_1) + V_j(\mathbf{r}_1) + V_i(\mathbf{r}_2) + V_j(\mathbf{r}_2) - r_{12}^{-1}) F^\circ_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad (19)$$

where

$$F^{o}_{ij}(\mathbf{r}_1, \mathbf{r}_2) = 2^{-\frac{1}{2}} \left(x_i(\mathbf{r}_1)\, x_j(\mathbf{r}_2) - x_j(\mathbf{r}_1)\, x_i(\mathbf{r}_2) \right) \quad (20)$$

with the obvious definition of the ε^{1}_{ij} as:

$$\varepsilon^{1}_{ij} = \left\langle F^{o}_{ij} \left| r_{12}^{-1} - V_i(\mathbf{r}_1) - V_j(\mathbf{r}_1) - V_i(\mathbf{r}_2) - V_j(\mathbf{r}_2) \right| F^{o}_{ij} \right\rangle \quad (21)$$

With the F^{1}_{ij} given by (19) the second order energy can be easily evaluated as a sum of individual pair energies ε^{2}_{ij}.

$$E2 = \sum_{ij} \varepsilon^{2}_{ij} \quad (22)$$

$$\varepsilon^{2}_{ij} = \left\langle F^{1}_{ij} \left| r_{12}^{-1} - V_i(\mathbf{r}_1) - V_j(\mathbf{r}_1) - V_i(\mathbf{r}_2) - V_j(\mathbf{r}_2) \right| F^{o}_{ij} \right\rangle - \varepsilon^{1}_{ij} \left\langle F^{1}_{ij} \left| F^{o}_{ij} \right\rangle \right. \quad (23)$$

It may be noted at this point that if for example the equation for the 1S1S pair function is explicitly written down as in (24) it is evident that this just the form which would be expected if it were assumed that the HF theory for the two-electron atomic sequence could be naively extended without formal derivation.

$$\begin{aligned} &(h^{o}(1) + h^{o}(2) - 2\,\varepsilon^{o}_{1s})\, F^{1}_{1s\uparrow 1s\downarrow} \\ &= (\varepsilon^{1}_{1s\uparrow 1s\downarrow} + V_{1s\uparrow}(\mathbf{r}_1) + V_{1s\downarrow}(\mathbf{r}_1) + V_{1s\uparrow}(\mathbf{r}_2) + V_{1s\downarrow}(\mathbf{r}_2) \\ &\quad - r_{12}^{-1})\, F^{o}_{1s\uparrow 1s\downarrow} \end{aligned} \quad (24)$$

Optimistically one might hope that this remarkable simplicity would be maintained to higher orders but unfortunately this is not true. As Ψ' is orthogonal to Ψ° then E3 is given by (25) and hence from this relation it can be written as (26) or (27).

$$E3 = \langle \Psi' | H' - E1 | \Psi' \rangle \tag{25}$$

Hence

$$E3 = \sum_{ij} \varepsilon^3_{ij;ij} + \sum_{ij;kl} \varepsilon^3_{ij;kl} \tag{26}$$

or

$$E3 = \sum_{ij} \langle F^1_{ij} | r_{12}^{-1} - V_i(\mathbf{r}_1) - V_j(\mathbf{r}_1) - V_i(\mathbf{r}_2) - V_j(\mathbf{r}_2) - \varepsilon^1_{ij} | F^1_{ij} \rangle + \text{'non-diagonal' terms.} \tag{27}$$

The first set of terms, those specified as 'diagonal', are entirely analogous to the ε^2_{ij} and are evaluated as one would expect if the naive pair model were exact. However the 'non-diagonal' contributions, which represent the lowest order component of effects beyond pair corr--elations i.e. three and four body contributions, are compounded of cross terms between the first order pair functions and hence it would appear necessary to discard the simple picture. The magnitude though of the non-diagonal components is quite obviously much smaller than those of the direct terms* and in the following discussion they are neglected.

* See for example Byron and Joachain (B20) or Bunge (B16) on this point.

Thus the correlation energy of a four-electron atomic system as calculated here is written as a sum of electron pair correlation energies each of which is formed from a second and third order contri--bution i.e.:

$$E_{corr} = \sum \varepsilon_{pair} = \sum_{ij} (\varepsilon^2_{ij} + \varepsilon^3_{ij}) \qquad (28)$$

Before examining the present attempts to discover whether (28) does give a reasonable approximation to the correlation energy for the atoms and ions studied here the manner in which the pair equations (19) are reduced to an appropriate form for practical computation is described in the next section.

3.3 Reduction of the pair equations to radial form

Thus far although a set of electron pair equations of fami--liar form have been derived the problem has yet to be further simplified before it can be attempted to solve for the first order function. Firstly the different types of electron pair are considered these being:- an inner shell pair $1S\uparrow 1S\downarrow$; an outer shell pair $2S\uparrow 2S\downarrow$; four intershell pairs $1S\uparrow 2S\uparrow$, $1S\downarrow 2S\downarrow$, $1S\uparrow 2S\downarrow$, $1S\downarrow 2S\uparrow$. It is fairly that the $1S\uparrow 2S\uparrow$ and $1S\downarrow 2S\downarrow$ pair energies will be identical as will those for the two remaining intershell pairs. Thus only four pair equations are required to be solved, these being discussed separately below for the intrashell and intershell pairs.

The equation for the 1S1S pair has already been written down as (24). Now $F^{o}_{1s\uparrow 1s\downarrow}$ has a singlet spin part and it is evident that $F^{1}_{1s\uparrow 1s\downarrow}$ can be factored as in (29), r_i here denoting all space vari-ables of the electron i.*

$$F^{1}_{1s\uparrow 1s\downarrow} = f_{1s1s}(r_1,r_2) \times 2^{-\frac{1}{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \qquad (29)$$

Hence (24) can be reduced to the spin-independent equation (30).

$$(\Omega(r_1,r_2) - 2\,\varepsilon^{o}_{1s})\, f_{1s1s}(r_1,r_2)$$
$$= (\varepsilon^{1}_{1s\uparrow 1s\downarrow} + V^{d}_{1s}(r_1) + V^{d}_{1s}(r_2) - r_{12}^{-1})\Phi_{1s}(r_1)\,\Phi_{1s}(r_2) \qquad (30)$$

where

$$\Omega(r_1,r_2) = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_1^2 - Z/r_1 - Z/r_2 + 2V^{d}_{1s}(r_1)$$
$$+ 2V^{d}_{1s}(r_2) + 2V^{d}_{2s}(r_1) + 2V^{d}_{2s}(r_2) - V^{e}_{1s}(r_1)$$
$$- V^{e}_{1s}(r_2) - V^{e}_{2s}(r_1) - V^{e}_{2s}(r_2) \qquad (31)$$

The pair function is now expanded in a Legendre series in the intervector

* Generally represented in bold face vector notation in 3.2, spin variables being also included in the appropriate cases in that section.

angle giving a set of radial equations entirely similar to those solved in the previous Chapter but which are omitted here for brevity.

The final problem which must be solved for this pair is the question of the orthogonality conditions (17). The removal of components of the 1s orbitals is trivial when equation (30) is considered but ensure that the equations are constrained so that the 2s orbitals do not enter into f_{1s1s} is more awkward. Fortunately only the S wave needs to be so treated and a solution of the general type (32) is required, $f^{(0)}_{1s1s}$ being say a variational trial function.

$$\begin{aligned} f^{(0)}(r_1,r_2) = {} & f^{(0)}_{1s1s} - \phi_{2s}(r_1)\left\langle \phi_{2s}(r_3) \,\middle|\, f^{(0)}_{1s1s}(r_3,r_2)\right\rangle \\ & - \phi_{2s}(r_2)\left\langle \phi_{2s}(r_3) \,\middle|\, f^{(0)}_{1s1s}(r_1,r_3)\right\rangle \\ & + \phi_{2s}(r_1)\,\phi_{2s}(r_2)\left\langle \phi_{2s}\;\phi_{2s} \,\middle|\, f^{(0)}_{1s1s}\right\rangle \end{aligned} \qquad (32)$$

For the 2S2S pair the final equations which are to be solved are entirely alike those for the inner shell pair but with for example ε^{o}_{2s} substituted for ε^{o}_{1s}.

For the intershell pairs the derivation is somewhat more complex due to a rather more complicated factorisation into space and spin parts.

For the $1S\uparrow 2S\uparrow$ pair $F^{1}_{1s\uparrow\, 2s\uparrow}$ has purely triplet spin dependence as in (33) and the equation for the space part $f_{1,1}$ is found fairly easily.

$$F^{1}_{1s\uparrow\,2s\uparrow} = f_{1,1}(r_1,r_2)\ a(1)\ a(2) \qquad (33)$$

$$\begin{aligned}(\Omega(r_1,r_2) &- \varepsilon^{o}_{1s} - \varepsilon^{o}_{2s})\ f_{1,1}(r_1,r_2) \\ = &(\varepsilon^{1}_{1s\uparrow\,2s\uparrow} + V^{d}_{1s}(r_1) + V^{d}_{1s}(r_2) + V^{d}_{2s}(r_1) + V^{d}_{2s}(r_2) - V^{e}_{1s}(r_1) \\ &- V^{e}_{1s}(r_2) - V^{e}_{2s}(r_1) - V^{e}_{2s}(r_2) - r_{12}^{-1}) \\ &\times 2^{-\frac{1}{2}}(\Phi_{1s}(r_1)\ \Phi_{2s}(r_2) - \Phi_{1s}(r_2)\ \Phi_{2s}(r_1)) \qquad (34)\end{aligned}$$

In addition for this type of pair there is no difficulty over orthog-onality as spin factors ensure this with respect to $\chi_{1s\downarrow}$ and $\chi_{2s\downarrow}$.

In contrast the $1S\uparrow 2S\downarrow$ and $1S\downarrow 2S\uparrow$ first order pairs cannot be expressed in terms of a pure singlet or triplet spin part and it is necessary to let them have the form (35)* which yields the equations (36) and (37) for the symmetric and antisymmetric space parts respectively.

$$\begin{aligned}F^{1}_{1s\uparrow\,2s\downarrow} = &f_{0,0}(r_1,r_2)\ (\alpha(1)\ \beta(2) - \alpha(2)\ \beta(1))/2^{\frac{1}{2}} \\ &+ f_{1,0}(r_1,r_2)\ (\alpha(1)\ \beta(2) + \alpha(2)\ \beta(1))/2^{\frac{1}{2}} \qquad (35)\end{aligned}$$

* These are the relevant equations for the $1S\uparrow 2S\downarrow$ pair function.

$$(\Omega(r_1,r_2) - \varepsilon^{o}_{1s} - \varepsilon^{o}_{2s})\, f_{0,0}(r_1,r_2)$$

$$= \tfrac{1}{2}(\varepsilon^{1}_{1s\uparrow 2s\downarrow} - r_{12}^{-1})\,(\Phi_{1s}(r_1)\,\Phi_{2s}(r_2) + \Phi_{1s}(r_2)\,\Phi_{2s}(r_1))$$

$$+ \tfrac{1}{2}(V^{d}_{2s}(r_1) + V^{d}_{1s}(r_2))\,\Phi_{1s}(r_1)\,\Phi_{2s}(r_2)$$

$$+ \tfrac{1}{2}(V^{d}_{1s}(r_1) + V^{d}_{2s}(r_2))\,\Phi_{1s}(r_2)\,\Phi_{2s}(r_1) \qquad (36)$$

$$(\Omega(r_1,r_2) - \varepsilon^{o}_{1s} - \varepsilon^{o}_{2s})\, f_{1,0}(r_1,r_2)$$

$$= \tfrac{1}{2}(\varepsilon^{1}_{1s\uparrow 2s\downarrow} - r_{12}^{-1})\,(\Phi_{1s}(r_1)\,\Phi_{2s}(r_2) - \Phi_{1s}(r_2)\,\Phi_{2s}(r_1))$$

$$+ \tfrac{1}{2}(V^{d}_{2s}(r_1) + V^{d}_{1s}(r_2))\,\Phi_{1s}(r_1)\,\Phi_{2s}(r_2)$$

$$+ \tfrac{1}{2}(V^{d}_{1s}(r_1) + V^{d}_{2s}(r_2))\,\Phi_{1s}(r_2)\,\Phi_{2s}(r_1) \qquad (37)$$

Taking (36) first a trial function (38) ensures that components of $\chi_{1s\downarrow}$ and $\chi_{2s\uparrow}$ are projected out.

$$= f^{(0)}_{0,0}(r_1,r_2) - \phi_{1s}(r_1)\,\langle\phi_{1s}(r_3)\,|\,f^{(0)}_{0,0}(r_3,r_2)\rangle$$

$$- \phi_{1s}(r_2)\,\langle\phi_{1s}(r_3)\,|\,f^{(0)}_{0,0}(r_1,r_3)\rangle$$

$$+ \phi_{1s}(r_1)\,\phi_{1s}(r_2)\,\langle\phi_{1s}\,\phi_{1s}\,|\,f^{(0)}_{0,0}\rangle$$

$$- \phi_{2s}(r_1)\,\langle\phi_{2s}(r_3)\,|\,f^{(0)}_{0,0}(r_3,r_2)\rangle$$

$$- \phi_{2s}(r_2)\,\langle\phi_{2s}(r_3)\,|\,f^{(0)}_{0,0}(r_1,r_3)\rangle$$

$$+ \phi_{2s}(r_1)\,\phi_{2s}(r_2)\,\langle\phi_{2s}\,\phi_{2s}\,|\,f^{(0)}_{0,0}\rangle \qquad (38)$$

If similar constraints are applied to $h_{1,0}$ then by straight-forward but extremely tedious manipulation (37) is found to be equivalent to (34) apart from the factor of root two. Hence the inter-shell correlation energy can be written as either (39) or (40).

$$E_{intershell} = 2\,\varepsilon_{1s\uparrow 2s\downarrow} + 2\,\varepsilon_{1s\uparrow 2s\uparrow} \qquad (39)$$

or

$$E_{intershell} = \varepsilon_{1S2S\ ^1S} + 3\,\varepsilon_{1S2S\ ^3S} \qquad (40)$$

Before discussing the results for the Be sequence it now only remains to describe the techniques used to solve the equations for the various components of the pair functions.

3.4 The solution of the radial equations

As for the two-electron sequence a combination of variational and numerical techniques was chosen for the determination of solutions of the partial differential equations which yield the partial wave components of each of the pair functions.

The 1S1S pair was of course easiest to deal with owing to the experience gained with the He series. The S wave was again computed variationally with an expansion in terms of simple functions of the 'CI' type as in (41).

$$U_0(r_1,r_2) = \sum_{m,n} (r_1^m r_2^n + r_1^n r_2^m) \exp(-\alpha r_1) \exp(-\alpha r_2) \qquad (41)$$

With regard to the orthogonality constraints it may be remarked that although (32) appears somewhat formidable initially, the Hermitean and other properties of the single-particle operators make it possible to express the matrix elements for the constrained function in little more complicated form than for the unconstrained counterpart.

For the other partial waves the equations were solved numeri--cally in the manner previously described on a 'square root' grid for 20(5)40 strips, the only difference from before being somewhat lengthier expressions for the Coulomb and exchange parts of the potentials.

For the 2S2S pair a similar approach to that for the inner shell pair was adopted with the main requirement being a rather more generous cutoff radius. As before the prescription was that R_{max} was taken as where, for the main lobe of the 2s orbital, P(r) falls to less than about 10^{-4}. For the S wave the trial function (41) was employed but with the 'physical' choice of exponents, Z-2.

Despite their small magnitude the intershell pair energies were the most troublesome to compute accurately. For the $\ell = 0$ waves two different types of function were tried viz. (42) and (43).

$$U_0(r_1,r_2) = \sum_{m,n} (r_1^m r_2^n \pm r_1^n r_2^m) \exp(-\alpha r_1) \exp(-\alpha r_2) \qquad (42)$$

$$W_0(r_1,r_2) = \sum_{m,n} (r_1^m r_2^n + r_1^n r_2^m) \times (\exp(-\alpha r_1 - \beta r_2) \pm \exp(-\alpha r_2 - \beta r_1)) \qquad (43)$$

Calculations of the Be S wave energies were executed using both (42) and (43) as it was of some interest for future work whether such a simple function as (42) could give reasonably accurate energies. The results were most informative:- For the triplet S wave (42) with 45 terms in the expansion and $\alpha = Z$ gave an energy of -0.00001356 a.u. while (43) with 44 terms and the physical choice of exponents Z, Z-2 yielded -0.00001352 a.u.. For the singlet S wave (42) with 44 terms and $\alpha = Z$ gave -0.001030 a.u. compared with -0.001024 a.u. using the alternative trial function with exponents as for the triplet. Thus it would appear that even very simple trial functions give good representations for the S part of electron pair functions provided that a reasonable number of terms is employed.*

For the calculation of the other partial waves the boundary conditions had to be examined carefully as it was found that if for example for Be a cutoff of 16.0 a.u. (that used for the 2S2S pair) was employed then the primitive $\varepsilon 2(\ell)$ and the extrapolants were not at all satisfactory. However if the inhomogeneity (44) in the radial equations

* There is a fairly substantial difference between the present results and those of Byron and Joachain (B20) for the intershell S wave energies. This is surprising since similar methods were used in both cases and no reason can be advanced for the discrepancy. Careful checking of the pro-grams failed to find any error in the work described here and it is to be noted that excellent agreement was obtained between the $\varepsilon 2(0)$ from (42) or (43) with varying expansion lengths, different exponents and alternative representations of the zeroth orbitals (the results from the Clementi 6 term basis set are -0.00001359 and -0.001033 a.u. which may be compared with those above computed from the 5 term expansion of the orbitals).

is inspected it is easy to see that this only has a substantial magnitude for either both r_1 and r_2 small or for one of the radii small and the other corresponding approximately to the principal maximum in P_{2s}.

$$\text{R.H.S.} = -2^{-\frac{1}{2}} \frac{r_<^{\ell}}{r_>^{\ell+1}} \left(P_{1s}(r_1)\, P_{2s}(r_2) \pm P_{1s}(r_2)\, P_{2s}(r_1)\right) \qquad (44)$$

Crudely these can be thought of as allowing respectively for correlation between an electron in the inner lobe of the 2s orbital and an electron in the inner shell and for longer range core-polarisation by an electron in the outer shell. It was found that cutoffs ranging from 4.5 to 10.0 a.u. gave negligibly different results for the Be calculations (N.B. the principal maxima in the P(r) are at about 0.25 and 2.0 a.u.). For the other systems R_{max} corresponding to the upper part of this range were used without apparent difficulty.

Lastly, as for the He sequence, the Hartree-Fock functions of Clementi (C7) were employed for the unperturbed orbitals.

3.5 Discussion for the Be sequence

The 1S1S, 2S2S and 1S2S pairs for $Li^-(1s^2 2s^2)$ to $Ne^{6+}(1s^2 2s^2)$ will now be discussed against a comparative background provided by earlier studies.

A The intrashell pairs ..... 1S1S and 2S2S

In Tables 3.1 and 3.2 the $\varepsilon 2(\ell)$, $\varepsilon 2$ and $\varepsilon 3$ are collected for the intrashell pairs for four of the systems studied.

The inner shell pair energy is remarkably stable as may be observed from Table 3.3 or from Figure 3.1 in which all of the pair energies are plotted versus atomic number. This may be contrasted with the behaviour for the analogous pair for the two-electron sequence for which, as demonstrated in Figure 3.2, the correlation energy increases in magnitude with Z. To attempt to find the reason for this difference between the two types of atomic system the values of the $\varepsilon 2(\ell)$ for Be and Be^{2+} and Ne^{6+} and Ne^{8+} contained in this and the previous Chapter (Tables 3.1 and 2.9 respectively) may be compared with the resulting observation that only the S wave contributions differ significantly. To enquire further into this question the orthogonality constraints on $F^1_{1s\uparrow\, 1s\downarrow}$ were relaxed with the results displayed in the third figure. From the latter it would appear that if the 2s orbitals were not pro--jected out, the computed 1S1S pair correlation energies would scarcely differ despite the 'field' effect of the outer pair. However when the 'exclusion' effect of the latter is taken into consideration the steady drop in the $\varepsilon 2(0)$ as Z increases is just sufficient to compen--sate for the greater importance of the other partial waves for the later members of the sequence.

The present results for the Be 1S1S pair appear to be in harmony with those of previous workers as can be seen from Table 3.4 in which a wide range of different calculations and estimates are collated. Probably the most reliable estimate of ε_{1S1S} is that of Bunge (B16) at -0.04261 a.u. with which the author's value of -0.04236 a.u. is fully consistent since higher orders of perturbation theory

Table 3.1 A comparison of the contributions to the correlation energy for the 1S1S pair for the Li^-, Be, B^+ and Ne^{6+} systems.

ℓ	Li^-	Be
0	-0.01318	-0.01247
1	-0.02128	-0.02248
2	-0.00344	-0.00355
3	-0.00098	-0.00101
4	-0.00038	-0.00039
5	-0.00017	-0.00018
6	-0.00009	-0.00009
7	-0.00005	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant 10$	-0.00005	-0.00005
Total ε_2	-0.03967	-0.04031
ε_3	-0.00267	-0.00205
$\varepsilon_2 + \varepsilon_3$	-0.04234	-0.04237

ℓ	B^+	Ne^{6+}
0	-0.01197	-0.01096
1	-0.02323	-0.02481
2	-0.00362	-0.00376
3	-0.00102	-0.00105
4	-0.00039	-0.00040
5	-0.00018	-0.00018
6	-0.00009	-0.00009
7	-0.00005	-0.00005
8	-0.00003	-0.00003
9	-0.00002	-0.00002
$\geqslant 10$	-0.00005	-0.00005
Total ε_2	-0.04066	-0.04141
ε_3	-0.00167	-0.00087
$\varepsilon_2 + \varepsilon_3$	-0.04233	-0.04228

Table 3.2 A comparison of the contributions to the correlation energy for the 2S2S pair for the Li^-, Be, B^+ and Ne^{6+} systems.

ℓ	Li^-	Be
0	-0.00307	-0.00226
1	-0.01151	-0.02214
2	-0.00241	-0.00382
3	-0.00081	-0.00119
4	-0.00034	-0.00048
5	-0.00017	-0.00023
6	-0.00009	-0.00012
7	-0.00005	-0.00007
8	-0.00003	-0.00004
9	-0.00002	-0.00003
$\geqslant$10	-0.00005	-0.00007
Total ε^2	-0.01856	-0.03044
ε^3	-0.00376	-0.00745
$\varepsilon^2 + \varepsilon^3$	-0.02232	-0.03789

ℓ	B^+	Ne^{6+}
0	-0.00232	-0.00245
1	-0.03021	-0.06383
2	-0.00449	-0.00570
3	-0.00133	-0.00156
4	-0.00053	-0.00060
5	-0.00025	-0.00027
6	-0.00013	-0.00014
7	-0.00007	-0.00008
8	-0.00005	-0.00005
9	-0.00003	-0.00003
$\geqslant$10	-0.00007	-0.00008
Total ε^2	-0.03947	-0.07480
ε^3	-0.01057	-0.02655
$\varepsilon^2 + \varepsilon^3$	-0.05005	-0.10135

Table 3.3 Pair and total correlation energies for the four-electron sequence.

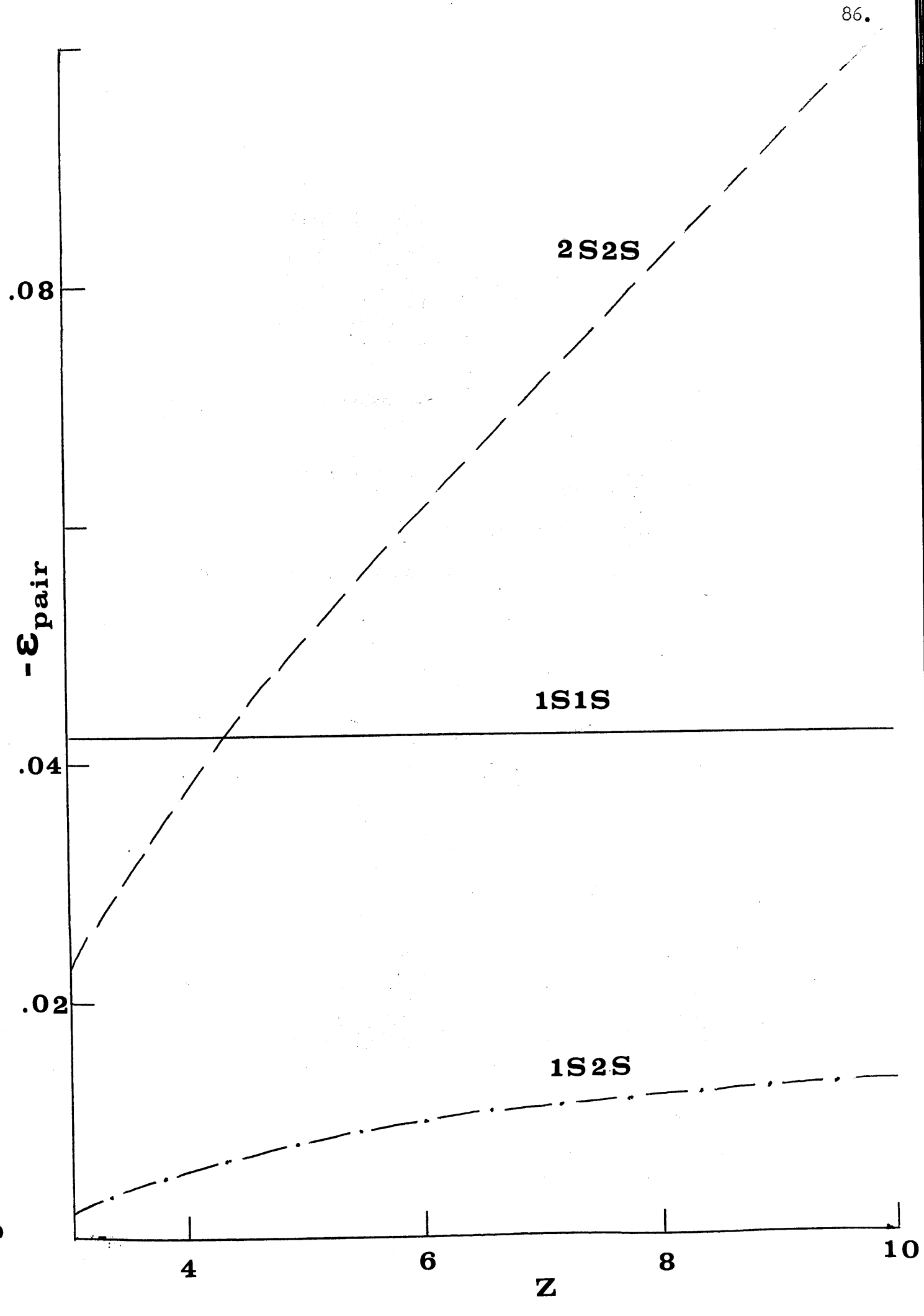
Z	$-\varepsilon_{1s1s}$	$-\varepsilon_{2s2s}$	$-\varepsilon_{1s2s}$	$-E_{corr}$	Exact*	%[a]
3.0	0.04234	0.02232	0.00247	0.06713	—	—
4.0	0.04236	0.03789	0.00607	0.08632	0.0944	91.4
5.0	0.04233	0.05005	0.00840	0.10078	0.1116	90.3
6.0	0.04230	0.06118	0.00995	0.11343	0.1268	89.5
7.0	0.04229	0.07159	0.01102	0.12491	0.1412	88.5
8.0	0.04228	0.08178	0.01187	0.13593	0.1551	87.6
9.0	0.04228	0.09164	0.01250	0.14642	0.1684	86.9
10.0	0.04228	0.10135	0.01299	0.15662	0.1814	86.3

* Taken from references (C6, B20).

[a] % of E_{corr} recovered in these calculations.

Figure 3.1

The variation of the 1S1S, 2S2S and 1S2S pair correlation energies with atomic number. All quantities are in atomic units (a.u.).


2S2S
1S1S
1S2S
.08
.04
.02
$-\varepsilon_{pair}$
4
6
8
10
Z

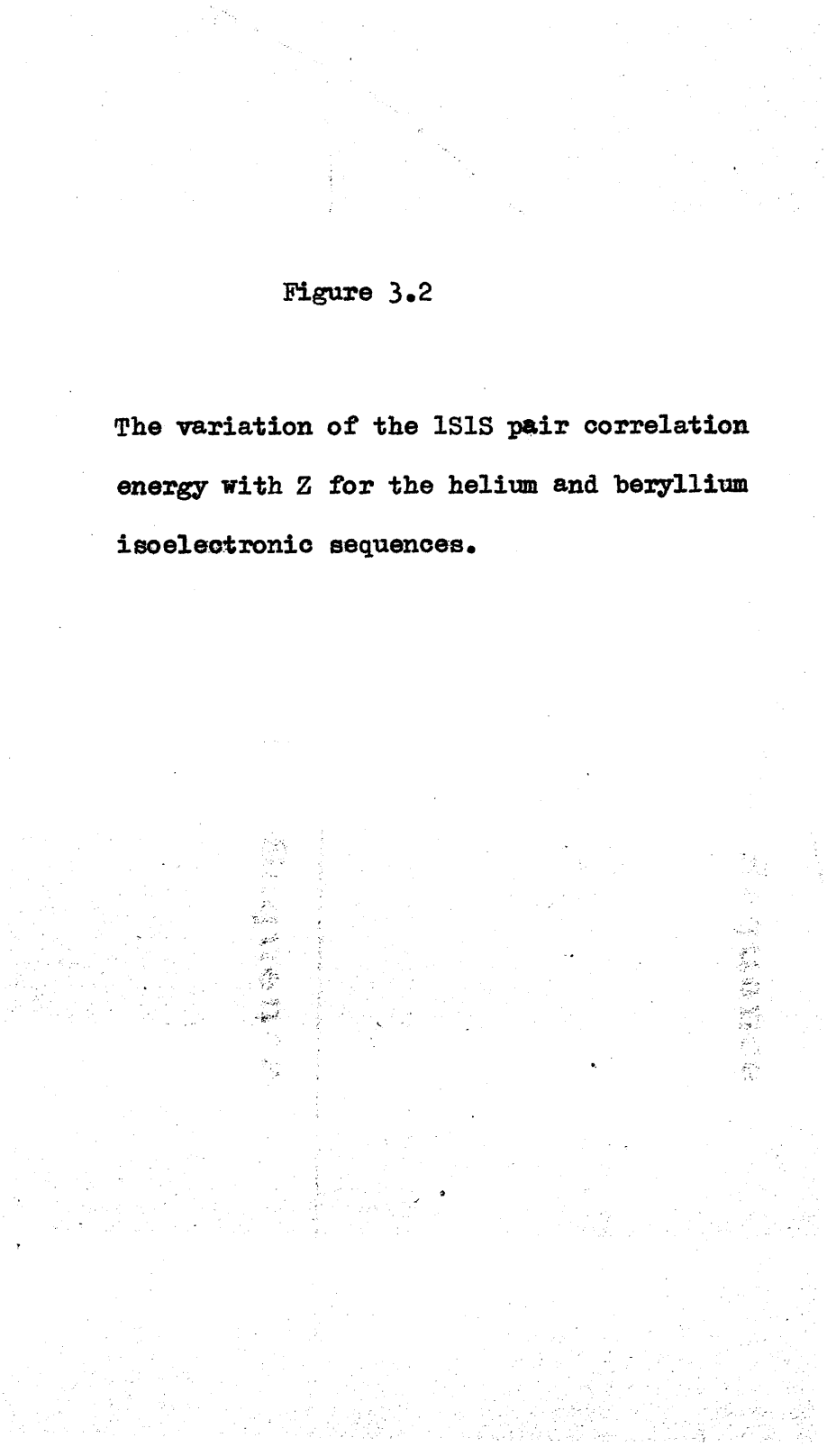


Figure 3.2

The variation of the 1S1S pair correlation energy with Z for the helium and beryllium isoelectronic sequences.

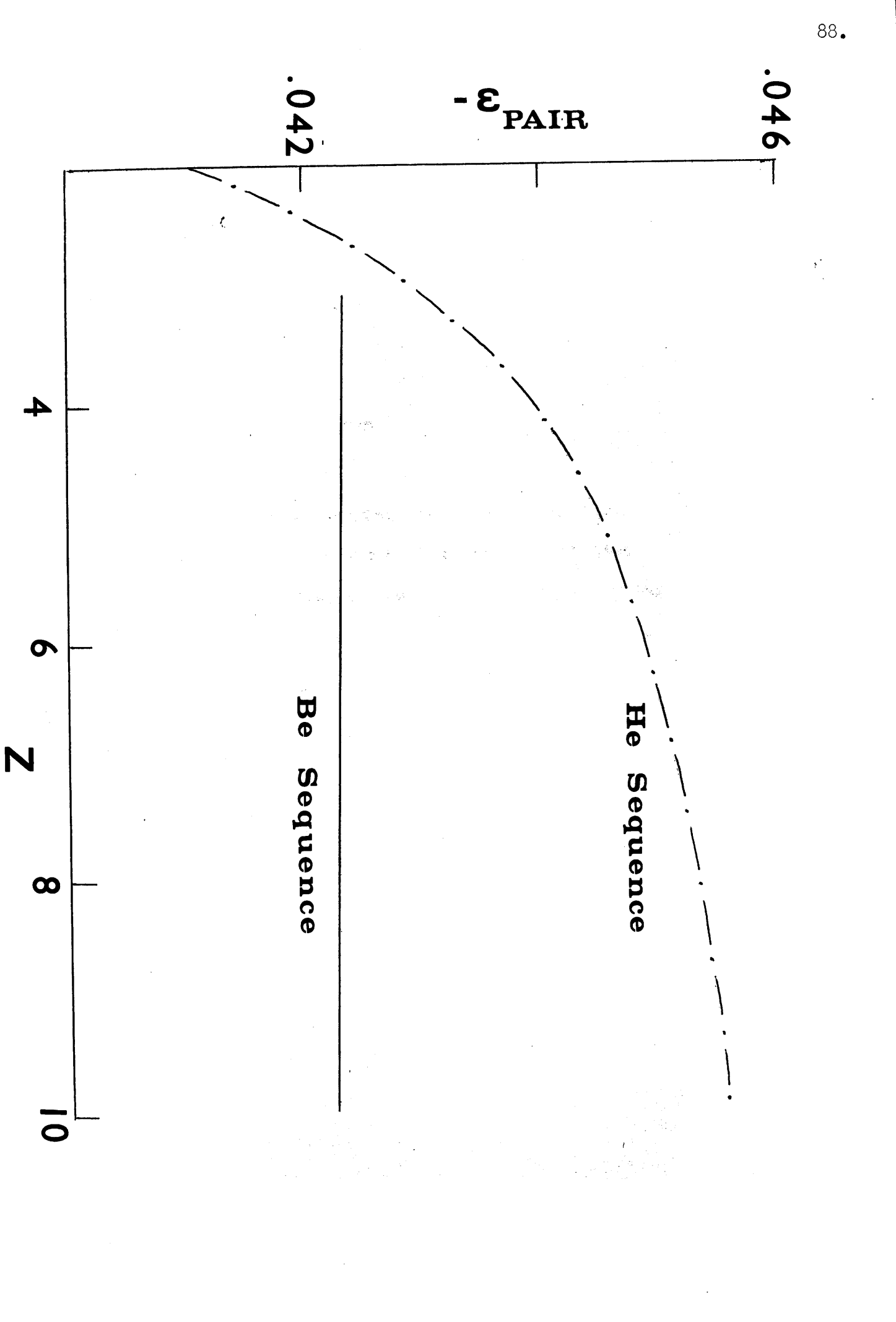

.042
$-\varepsilon_{PAIR}$
.046
4
6
8
10
Z
Be Sequence
He Sequence

Figure 3.3

The S wave energies for:- A the helium series; B the beryllium sequence without orthogonalisation to the 2s orbitals; C the beryllium sequence with projection of the 2s orbitals.

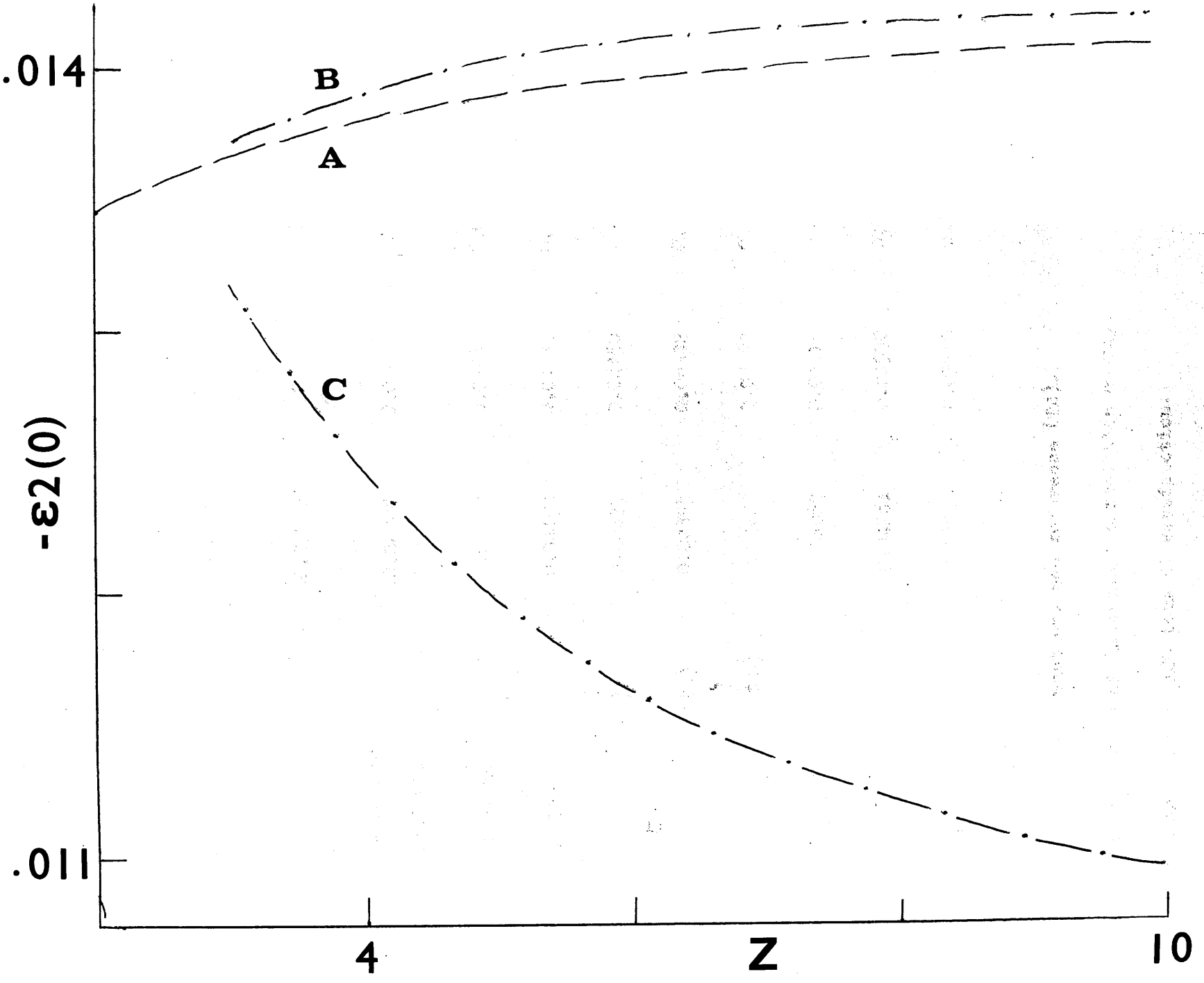

.014
.011
B
A
C
-ε2(0)
4
Z
10

Table 3.4 A comparison of pair correlation energies for beryllium.

Author(s)	$-\varepsilon_{1S1S}$	$-\varepsilon_{2S2S}$	$-\varepsilon_{1S2S}$
Watson[1] (W2)	0.03759	0.04178	0.00505
Geller, Taylor & Levine[2] (G1)	0.04208	0.04438	0.006
Kelly (K7, K8)	0.04212	0.04488	0.00497
Nesbet (N2)	0.04183	0.04535	0.00586
Szasz & Byrne (S29)	0.04235	0.04450	—
Tuan & Sinanoglu (T4)	0.04395	0.04392	0.00648
Byron & Joachain (B20)	0.04247	0.04482	0.00524
Bunge[3] (B16)	0.04087	0.04510	0.00524
Bunge[4]	0.04261	0.04550	0.00530
Present work	0.04236	0.03789	0.00606

[1] Analysis of CI function. See reference (T4).

[2] Estimated value of intershell correlation energy.

[3] From analysis of 180 term CI wavefunction.

[4] Estimated limiting pair energies.

have not been considered here. However the close similarity between the second and third order energies for this pair in the two and four electron series suggests that the contribution from higher orders will be very small i.e. about the same magnitude as the difference between the sum through E3 and the exact energy for Be^{2+} ——— -0.00037 a.u. from the work of Chapter 2. Byron and Joachain's estimate of -0.00029 a.u. is fully in accord with this and there seems to be little doubt that a result very close to Bunge's extrapolation would be achieved if the pair model were carried further. As will be discussed in a later section the convergence through to third order appears to be most satis--factory with for any of the systems 99% or better of the pair correla--tion energy recovered.

In contrast to above, the values obtained for the other intrashell pair energy are considerably deficient. This is a manifesta--tion of the $2s^2$ — $2p^2$ near-degeneracy effect which is evident in the dominance of the p wave contribution to $\varepsilon 2$ and which becomes increasingly striking with Z. CI is very efficient in accounting for the former but however perturbation theory is only slowly convergent and hence fourth and higher energies would be required to give very accurate results. Nevertheless even for the larger values of Z 80% or more of the 2S2S pair energy is estimated to have been recovered. Neither is the quali--tative behaviour of ε_{2S2S} apparently distorted and the near linear increase in this quantity with atomic number follows closely the pattern predicted some years ago by Linderburg and Shull (L9) and examined more recently by Alper (A8).

B The intershell pairs 1S2S

As well as posing the most difficult computational problems the intershell pairs give the most interesting results presented here although they account for less than 10% of the correlation energy for any of the atoms studied here.

In Tables 3.5 and 3.6 details are given for the $\varepsilon 2$ and $\varepsilon 3$ as for the other pairs but it is the comparison with earlier studies in Table 3.4 that is most informative. It is obvious that the intershell correlation energy for Be calculated in this work is some--what larger in magnitude than that obtained by many previous researchers. However a substantial amount of evidence can be marshalled to indicate that this is in fact correct:-

1/ The results of Byron and Joachain (B20) were calculated using a simple variational function of the type (43) for all partial waves. Comparison of their work on the 1S2S pairs for He (B19) with the accurate numerical results of Winter (W12) (confirmed by the author in Chapter 2) indicate that very large errors must be expected in the partial wave energies other than for $\ell = 0$. Overall an error of at least 5% in the second order contribution is to be expected with the probability of this being much higher as the He computations were performed with trial functions containing many more terms. It is unlikely that a countervailing reduction in the magnitude of the third order energy could compensate for this factor.

2/ The recent HF perturbation calculations of Pan and King (P1) give a calculated or estimated upper bound to $\varepsilon 2(1S2S\ ^1S)$ and $\varepsilon 2(1S2S\ ^3S)$ of -0.00300 and -0.00071 a.u. which may be compared with

Table 3.5 A comparison of contributions to the correlation energy for the $1S\uparrow 2S\uparrow$ pair for the Li^-, Be, B^+ and Ne^{6+} systems.

ℓ	Li^-	Be
0	-0.000005	-0.000014
1	-0.000280	-0.000663
2	-0.000021	-0.000050
3	-0.000003	-0.000008
4	-0.8×10^{-6}	-0.000002
5	-0.3×10^{-6}	-0.6×10^{-6}
6	-0.1×10^{-6}	-0.2×10^{-6}
7	-0.4×10^{-7}	-0.1×10^{-6}
8	-0.2×10^{-7}	-0.5×10^{-7}
9	-0.1×10^{-7}	-0.3×10^{-7}
$\geqslant 10$	-0.1×10^{-7}	-0.4×10^{-7}
Total $\varepsilon 2$	-0.000310	-0.000738
$\varepsilon 3$	-0.000057	-0.000104
$\varepsilon 2 + \varepsilon 3$	-0.000366	-0.000843

ℓ	B^+	Ne^{6+}
0	-0.000020	-0.000032
1	-0.000908	-0.001406
2	-0.000070	-0.000108
3	-0.000011	-0.000018
4	-0.000003	-0.000004
5	-0.000001	-0.000001
6	-0.3×10^{-6}	-0.5×10^{-6}
7	-0.1×10^{-6}	-0.2×10^{-6}
8	-0.7×10^{-7}	-0.1×10^{-6}
9	-0.4×10^{-7}	-0.6×10^{-7}
$\geqslant 10$	-0.5×10^{-7}	-0.8×10^{-7}
Total $\varepsilon 2$	-0.001013	-0.001570
$\varepsilon 3$	-0.000116	-0.000091
$\varepsilon 2 + \varepsilon 3$	-0.001128	-0.001661

Table 3.6 A comparison of the contributions to the correlation energy for the $1S\uparrow 2S\downarrow$ pair for the Li^-, Be, B^+ and Ne^{6+} systems.

ℓ	Li^-	Be
0	-0.000199	-0.000522
1	-0.000483	-0.001241
2	-0.000059	-0.000148
3	-0.000015	-0.000041
4	-0.000006	-0.000015
5	-0.000003	-0.000007
6	-0.000001	-0.000003
7	-0.7×10^{-6}	-0.000002
8	-0.4×10^{-6}	-0.000001
9	-0.3×10^{-6}	-0.000001
$\geqslant 10$	-0.7×10^{-6}	-0.000002
Total $\varepsilon 2$	-0.000768	-0.001993
$\varepsilon 3$	-0.000100	-0.000201
$\varepsilon 2 + \varepsilon 3$	-0.000868	-0.002193

ℓ	B^+	Ne^{6+}
0	-0.000736	-0.001151
1	-0.001772	-0.002935
2	-0.000228	-0.000379
3	-0.000059	-0.000099
4	-0.000022	-0.000036
5	-0.000010	-0.000016
6	-0.000005	-0.000008
7	-0.000003	-0.000005
8	-0.000002	-0.000003
9	-0.000001	-0.000002
$\geqslant 10$	-0.000003	-0.000005
Total $\varepsilon 2$	-0.002840	-0.004638
$\varepsilon 3$	-0.000232	-0.000195
$\varepsilon 2 + \varepsilon 3$	-0.003072	-0.004833

the present values of -0.00324_8 and -0.00073_8 a.u. and those of Byron and Joachain of -0.00247 and -0.00070 a.u.. Unfortunately the former authors did not calculate any contributions above second order but it is evident that to give a total intershell correlation energy in the region of the commonly accepted value for this quantity of -0.0050 to -0.0053 a.u. would require an improbably fast convergence of the perturbation series. Similar considerations apply for B^+ with overall for these two systems good agreement between the values of $\varepsilon 2_{1S2S}$ from this work and from that of Pan and King.*

3/ The Bethe-Goldstone calculation of Nesbet (N2) gives -0.000813 and -0.002119 a.u. for the $1S\uparrow 2S\uparrow$ and $1S\uparrow 2S\downarrow$ pairs com--pared with -0.000843 and -0.002193 a.u. from this study. The agreement, although good, would probably be even better if a larger basis set were used in the BG calculations, it being noticeable that the difference in the two sets of results is a uniform $3\frac{1}{2}\%$. Differences in formalism may of course invalidate the above comparison but however the analysis of Bunge (B16) implies that the BG and other types of pair theory give results for Be which do not vary greatly. Finally before leaving this question it may be noted that the work of Viers, Harris and Schaefer (V3) on the calculation of symmetry-adapted and standard BG pairs for the Ne atom suggests that the problem of overshoot of the true correl--ation energy mentioned in the Introduction should not be a serious difficulty for the beryllium system.

* These authors place tentative error bounds of 0.0002 and 0.00002 a.u. on their $\varepsilon 2$ for the singlet and triplet pairs respectively.

4/ Lastly it can be seen from Table 3.4 that an analysis of Watson's CI function (W2, T4) implies an error in the intershell corr--elation energy of only about 5% assuming that the correct value for this quantity is -0.0053 a.u., while the deviations for the inner and outer shell pairs are 12% and 8% respectively. Yet a large amount of work indicates that CI for intershell pairs is only slowly convergent (N2, B16, M6, W6) indirectly suggesting that the 1S2S correlation energy is larger in magnitude than the above value. However this is the most tenuous piece of evidence as it is rather obscure as to which contributions are considered as intershell effects in this analysis.

On consideration of the above points and of the present work it can almost certainly be said that the intershell correlation energy for Be will exceed the estimate of Bunge of -0.0053 a.u. by an apprec--iable amount.[1] If the value of about -0.06 a.u. indicated here is confirmed it will interestingly vindicate the semi-empirical calcula--tion of Tuan and Sinanoglu (T4) which gave -0.00648 a.u. for ε_{1S2S}.

As for the intrashell pairs the intershell correlation energy varies in a quite definite way with Z as can be seen from the first Figure. However it is also informative to plot this quantity

[1] It is difficult to give judgement on this rather discouraging result without knowledge of how the CI energy was decomposed into pair cont--ributions e.g. how non-diagonal terms were partitioned. Additionally extrapolation of limiting pair energies from an analysis of a, necess--arily, incomplete CI computation may not be an entirely valid procedure especially where a small quantity such as ε_{1S2S} is concerned. Similar strictures may of course apply to the pair energies derived from Watson's function.

versus 1/Z and, as can be observed from Figure 3.4, for higher values of the atomic number an almost linear relationship is found. Miller and Ruedenberg (M6) have noted this phenomenon within an augmented separated pair formalism.

Finally before leaving this section it is appropriate to comment on the convergence of the partial wave expansion for the various pairs. As can be seen from Figure 3.5 it is as ℓ^{-4} for space symmetric functions and ℓ^{-6} for the antisymmetric portion of the intershell pairs thus confirming the extension of Schwartz's conjecture from two-electron atoms to at least these many-electron systems.

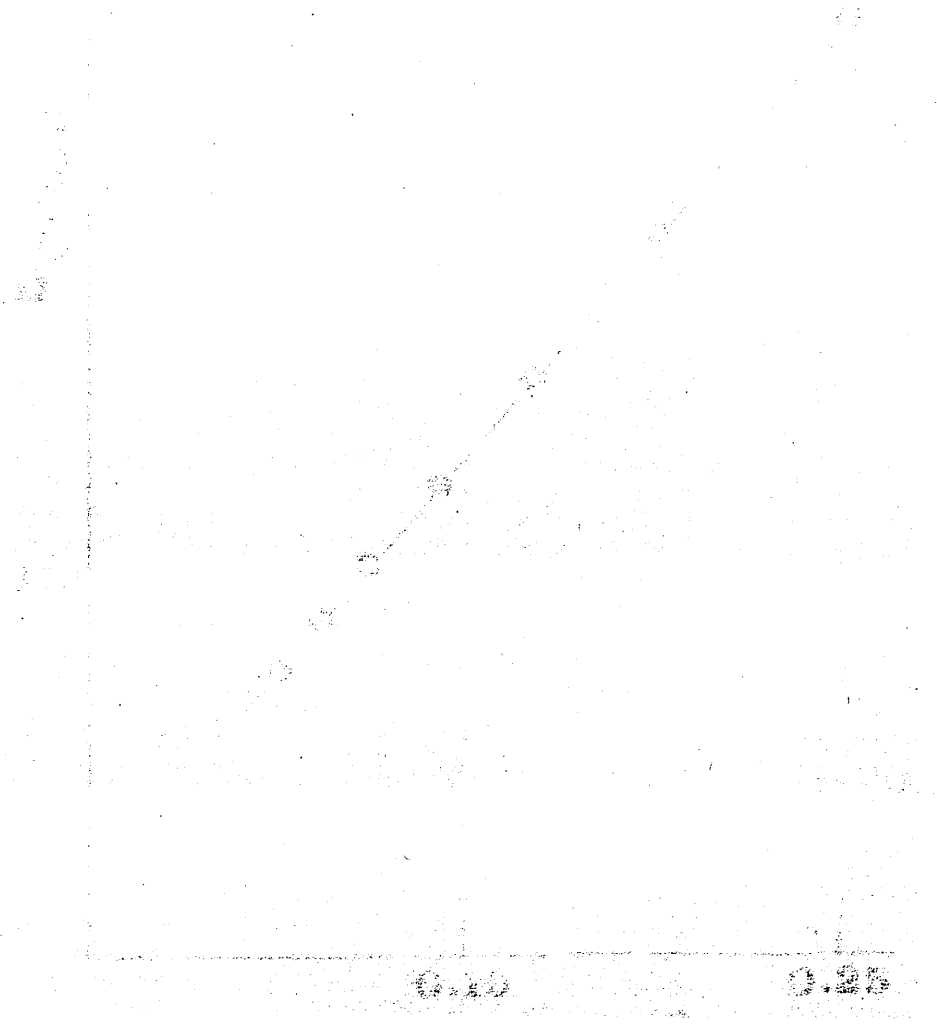
C A general consideration of the convergence of the HF theory.

Two questions should be asked about these calculations:- How well do these computations with other ab initio calculations ? Where does the biggest error occur and how can the results be improved either by further calculation or by plausible extrapolation ?

In Table 3.7 an extensive range of other calculations is compared with the present work for the case of beryllium. For this atom the error in the HF perturbation calculations through to E3 can be con--sidered to be of chemical accuracy i.e. it is approximately 0.0078 a.u. or 5 Kcals. Broadly it would appear that this is only substantially improved on by studies which entail a relatively much greater computa--tional effort e.g. the massive CI calculation of Bunge (B16). One advantage of the scheme described in this Chapter is that it is fairly easy to locate the sources of the deficiencies in the calculation and hence estimate the required corrections to them. There can be no doubt about the largest of these in this case viz. the slow convergence of the

Figure 3.4

The intershell correlation energy for the beryllium sequence as a function of Z^{-1}.



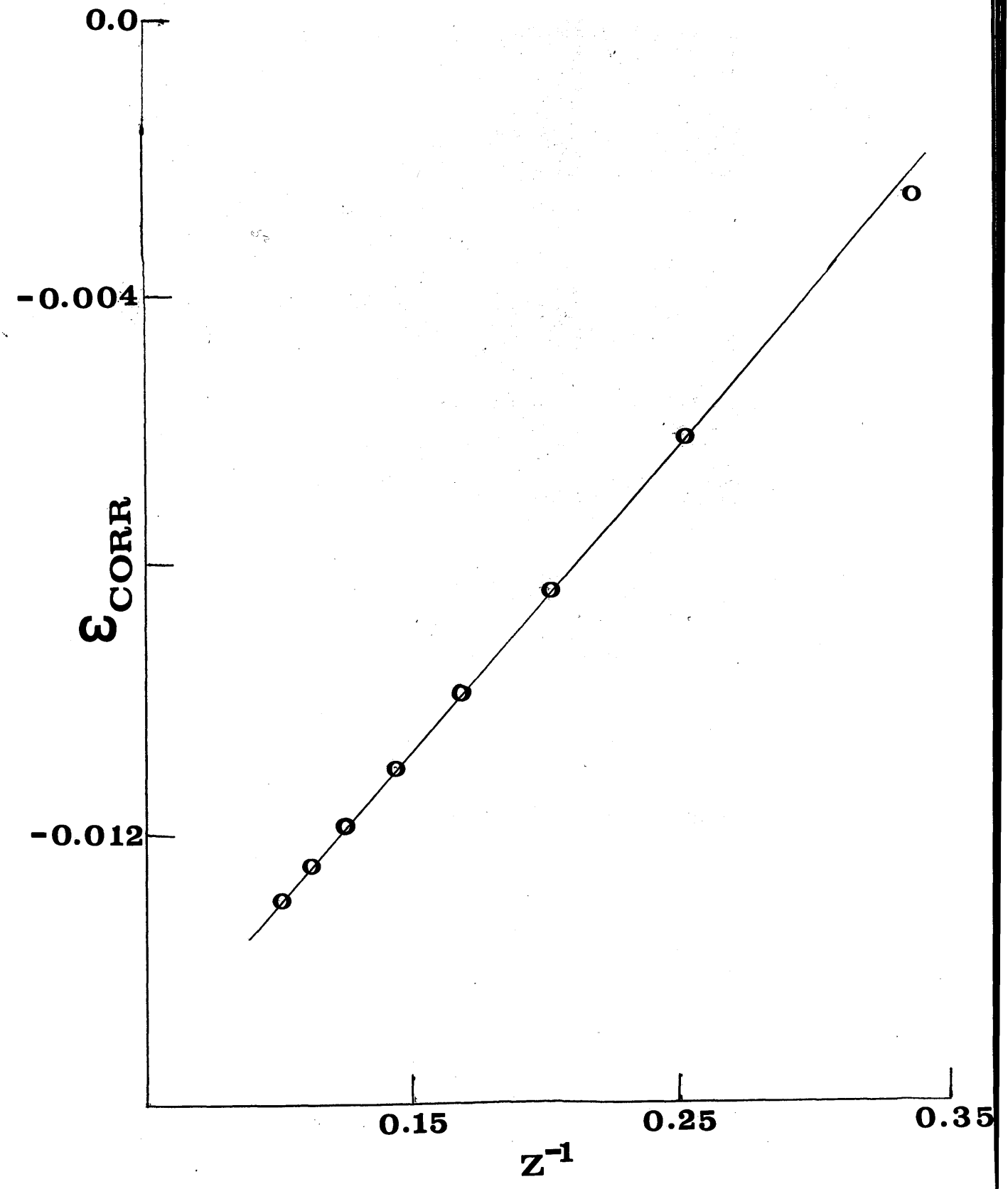

0.0
-0.004
-0.012
ω_{CORR}
0.15
0.25
0.35
Z^{-1}

Figure 3.5

Plots of $\log(|\varepsilon_2(\ell)|)$ versus $\log(\ell)$ for the 1S1S, 2S2S, 1S2S ^{1}S and 1S2S ^{3}S pairs in Be. The proposed asymptotic gradient of -4 or -6 is shown in each case.

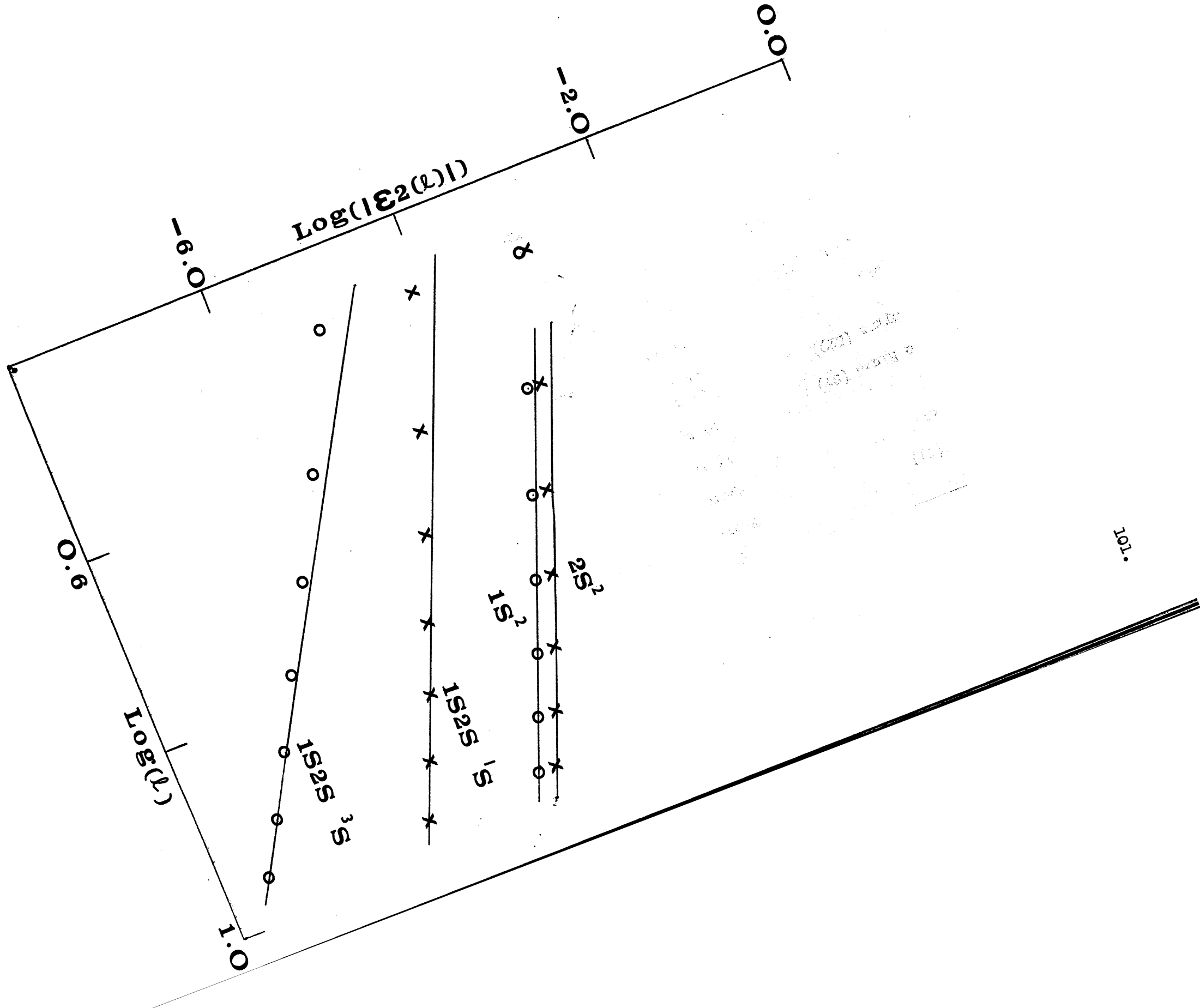

-6.0
Log(|ε2(ℓ)|)
-2.0
0.0
0.6
Log(ℓ)
1.0
1S2S 3S
1S2S 1S
1S2
2S2
101.

Table 3.7 A comparison of values of the total non-relativistic energy for Be derived from a variety of ab initio calculations. Quoted values have all been arbitrarily truncated to 6 figures.

Author (s)	Method	Energy	% correlation energy
Clementi (C7)	Restricted Hartree-Fock	-14.5730	0.0
Knight (K11)	Hydrogenic perturbation theory	-14.6448	76.2
Karl (K2)	13 term Hylleraas wavefunction	-14.6497	81.4
Sabelli & Hinze (S1)	10 tern MCSCF	-14.6546	86.5
Szasz & Byrne (S29)	27 term Hylleraas wavefunction :- no intershell terms	-14.6565	88.5
Watson (W2)	37 term CI	-14.6574	89.5
Gentner & Burke (G2)	25 term Hylleraas wavefunction :- intershell terms	-14.6579	90.0
Byron & Joachain (B20)	HF perturbation theory through E3	-14.6585	90.6
This work	HF perturbation theory through E3	-14.6593	91.4
Handy (H2)	Transcorrelated function	-14.6596	91.7
Weiss (W6)	55 term CI	-14.6609	93.2
Bunge (B16)	180 term CI	-14.6642	96.7
Nesbet (N2)	Bethe-Goldstone study	-14.6651	97.7
Byron & Joachain (B20)	HF perturbation theory through E5	-14.6655	98.0
Sims & Hagstrom (S19)	107 term combined CI/Hylleraas wavefunction	-14.6665	99.0

perturbation theory for the 2S2S pair due to the $2s^2$ -- $2p^2$ near-degeneracy effect. In Table 3.8 for all the pairs $\varepsilon 2$, $\varepsilon 3$ and $\% |\varepsilon 3/\varepsilon 2|$ are listed for the atoms and ions examined. The convergence for the inner and intershell pairs is fast and improves with increasing Z but the reverse is true for the outer shell. As far as the total correlation energy is concerned the 2S2S pair energy dominates for the later members of the sequence and thus a smaller percentage of the corr--elation energy is expected to be recovered as the species become more highly ionised. This is observed in Table 3.3. One may comment that the slowness of the convergence of the HF perturbation series for the 2S2S pair is more than just a matter of "loose" binding ..... actually as the binding becomes tighter the convergence becomes slower.

Within the approximation that the correlation energy can be partitioned as a sum of pair correlation energies it is enlightening to attempt to construct this quantity from the present and other accurate pair studies. For Be, as previously discussed, a value of -0.04261 a.u. would appear to be appropriate for the 1S1S pair correlation energy. In addition Bunge's (B16) estimate of -0.04550 a.u. for ε_{2S2S} seems about right. His suggestion that the contributions from sixth and higher orders in perturbation theory are smaller than the 0.001 — 0.002 a.u. suggested by Byron and Joachain is plausible since a sizeable proportion of E4 and E5 arises from the 1s1s, 2s2s unlinked cluster. Now if the author's value of -0.00607 a.u. is taken for ε_{1S2S} then this gives a total of -0.0942 a.u. in good agreement with the exact non-relativistic value of -0.0943 to -0.0944 a.u. (C6, B20, M6). It would thus appear that the discrepancy of about 0.0009 a.u. found by Bunge between his upper bound and the accepted non-relativistic energy can be explained in part

Table 3.8 An analysis of the contribution of ε2 and ε3 to the pair correlation energies and to the total correlation energy.

Z	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
1S1S								
ε2	-0.03967	-0.04031	-0.04066	-0.04089	-0.04107	-0.04121	-0.04132	-0.04141
ε3	-0.00267	-0.00205	-0.00167	-0.00141	-0.00122	-0.00108	-0.00096	-0.00087
%ε3/ε2	6.7	5.1	4.1	3.4	3.0	2.6	2.3	2.1
2S2S								
ε2	-0.01856	-0.03044	-0.03947	-0.04731	-0.05445	-0.06150	-0.06822	-0.07480
ε3	-0.00376	-0.00745	-0.01057	-0.01388	-0.01714	-0.02027	-0.02342	-0.02655
%ε3/ε2	20.2	24.5	26.8	29.3	31.5	33.0	34.3	35.5
1S2S								
ε2	-0.00216	-0.00546	-0.00771	-0.00925	-0.01035	-0.01123	-0.01189	-0.01242
ε3	-0.00032	-0.0061	-0.00070	-0.00070	-0.00068	-0.00064	-0.00061	-0.00057
%ε3/ε2	14.8	11.2	9.1	7.6	6.6	5.7	5.1	4.6
Total								
E2	-0.06039	-0.07621	-0.08784	-0.09745	-0.10587	-0.11394	-0.12143	-0.12863
E3	-0.00675	-0.01011	-0.01294	-0.01599	-0.01904	-0.02199	-0.02499	-0.02799
% E3/E2	11.2	13.3	14.7	16.4	18.0	19.3	20.6	21.8

at least by an inadequate treatment of intershell correlation.*

The above result may of course be fortuitous but it would appear worthwhile to try to estimate the correlation energy for B^+ in the same manner. For the 1S1S pair the present results plus an error estimate (from the two-electron work) for the higher order corrections imply a pair energy of about -0.0425 to -0.0426 a.u. which compares well with Byron and Joachain's value of -0.04248 a.u.. For the intershell correlation energy the value of -0.00840 a.u. from Table 3.3 is chosen. For the outer shell either the SOC estimate of Weiss (W7) of -0.0609 a.u. can be taken or the HF perturbation calculation of Byron and Joachain of -0.05955 a.u. with a correction for higher orders of about 0.001 a.u.. The minimum or maximum value of the correlation energy of -0.1119 a.u. or -0.1114 a.u. probably both lie within the error bounds on the exact value of -0.1116 a.u. (C6, B20). Analogous arguments for C^{2+} suggest a correlation energy of about -0.1270 a.u. which again is in harmony with the exact value of -0.1268 a.u..

Lastly there is the important question of the electron affinity of Li. On the basis of a Hartree-Fock calculation this is eva--luated to be -0.12 eV (C7) but taking the exact non-relativistic energy of Li as -7.47807 a.u. (W6) a value of 0.47 eV is obtained using the total energy for Li^- calculated here. The latter is much closer to the experimental data cited in the literature:- the value of Ya'Akobi (Y1) at 0.6 eV or the alternative of Scheer and Fine (S3) of 0.65 — 1.05 eV with the value probably lying in the upper part of the range. By

* The suggestion that the discrepancy may be due to the inadequate calculation of the relevant relativistic correction is not convincing as this quantity would appear to be of too small a magnitude for even substantial errors in it to appreciably affect the estimate of the non-relativistic energy. (it is about 1% of the correlation energy).

forgoing rigour and arguing intuitively, but probably accurately, as in the previous paragraphs the value of 0.47 eV can be improved upon. The error in ε_{2S2S} can be estimated to most probably lie between 0.1 and 0.13 eV and it is unlikely that other deficiencies in the pair energies contribute more than 0.02 eV thus suggesting an electron affinity of about 0.6 eV. Various model potential studies, notably that of Victor and Laughlin (V2) who give a list of previous theoretical treatments of this problem, strengthen the view that the first experimental result is to be preferred. This question will be returned to in Chapter 9 where pseudopotential approaches will be considered in conjunction with the type of numerical methods used in this work so far.

3.6 Extensions to other systems

A relevant inquiry concerning the work in this Chapter is whether the techniques used here for the Be series can be applied to other many-electron atoms ?

Consider first the next closed shell system which is Ne. For this atom nine pair equations have to be solved viz. the four treated for Be, two each for the 1S2P and 2S2P pairs and three 2P2P pairs. Clearly the new types of pairs will present many problems not yet encoun-tered for the purely S pairs but these should not be insurmountable. For example Winter and McKoy (W17) have solved pair equations for nS2P pairs in He without apparently any great difficulty though full results have yet to be published. In Table 3.9 some results for the partial wave contributions to $\varepsilon 2$ for the 1S1S, 2S2S and 1S2S pairs of Ne are collected, these having been computed in a similar manner to those for the four-electron series. For the most part it can be seen that the

Table 3.9 The values of the partial wave contributions to $\varepsilon 2$ for the $1s\uparrow 1s\downarrow$, $2s\uparrow 2s\downarrow$, $1s\uparrow 2s\downarrow$ and $1s\uparrow 2s\uparrow$ pairs of Ne.

ℓ	$1s\uparrow 1s\downarrow$	$2s\uparrow 2s\downarrow$
0	-0.01211	-0.00293
1	——	——
2	-0.00377	-0.00492
3	-0.00105	-0.00133
4	-0.00040	-0.00051
5	-0.00018	-0.00024
6	-0.00009	-0.00012
7	-0.00005	-0.00007
8	-0.00003	-0.00004
9	-0.00002	-0.00003
$\geqslant 10$	-0.00005	-0.00007

ℓ	$1s\uparrow 2s\downarrow$	$1s\uparrow 2s\uparrow$
0	-0.000837	-0.000023
1	——	——
2	-0.000252	-0.000074
3	-0.000065	-0.000012
4	-0.000023	-0.000003
5	-0.000010	-0.000001
6	-0.000005	-0.4×10^{-6}
7	-0.000003	-0.2×10^{-6}
8	-0.000002	-0.7×10^{-7}
9	-0.000001	-0.4×10^{-7}
$\geqslant 10$	-0.000003	-0.5×10^{-7}

the $\varepsilon 2(\ell)$ do not differ greatly between the four and ten electron sequences but however no $\varepsilon 2(1)$ are included in Table 3.9 as the most appropriate method for dealing with these components is still being investigated:- It is necessary to constrain the F^1_{ij} to be orthogonal to the χ_{2p} for the Ne system, this factor appearing in the p wave for the pairs already dealt with. This orthogonality condition poses prob--ably the most difficult problem in the extension of the HF perturbation theory to larger systems. It is fairly easy to see a number of possible ways to deal with it but it is vital to have a computationally efficient and accurate scheme as it is energetically very important for certain of the pairs e.g. for the 2S2S pair it seems likely that the p wave contribution will be about -0.002 a.u. or less compared with -0.064 a.u. in Ne^{6+} the reduction, due mainly to the exclusion effect of the 2p orbitals, being no less than thirtyfold.

Overall it seems possible that if the HF perturbation series is accurately computed through E3 then the calculated correlation energy will be only a few per cent in error. For the Be sequence the principal deficiency was the slow convergence of the 2S2S pair energy owing to the near-degeneracy effect but for Ne this will not be a problem for the reasons mentioned above. There is of course the possib--ility that similar difficulties will be encountered with some of the other pairs but the work of Pan and King (P1), who estimate that about 88% of the correlation energy is recovered in second order (about the same proportion as in He), suggests that this is not the case. In addition, although three and four body effects are expected to become more important as the number of electrons in the system increases, the result of Bunge and Peixoto (B17) from a CI study that these contribute 1% or less to the correlation energy implies that the pair model can

probably be usefully employed at least as far as the start of the Second Row. It is interesting to note that in this last calculation CI including a huge number of configurations recovered only 89% of E_{corr} or about the same as was found from E2 in HF perturbation theory. The reason for this somewhat discouraging result is the slow convergence for configurations of higher azimuthal quantum number, Bunge and Peixoto estimating that about 8% of the correlation energy arises from configurations involving g,h,i and higher excitations. Similar conclus--ions are evident from the symmetry-adapted pair calculations of Viers, Harris and Schaefer (V3). Thus numerical techniques of the type used here are probably the most tractable way of accurately evaluating these contributions, it being quite practical to solve a large number of equations even when coupled as can be seen from the next Chapter and from the work of Winter (W13) on the hydride ion.

For open shell systems the prospects are equally inviting although the development of the theory will be more difficult especially as far as the definition of the HF potential is concerned. Alternatively some other perturbation scheme such as those employed by Schulman, Lee, Hui and Musher, and Schulman and Lee for Li could be employed (S6, S5). Hence the accurate calculation of the electronic energy of all atoms through at least to Mg seems an entirely feasible project using either numerical methods or probably more economically using a combination of numerical and variational techniques as here.

3.7 Conclusions

In this Chapter it has been seen how simple numerical methods as described in Chapter 2 could be further developed to solve, in

conjunction with straightforward variational techniques, the relatively complicated problems arising in the perturbation theory of four-electron atomic systems. In particular the small, but important, contributions of the intershell terms were accurately evaluated and found to be somewhat larger in magnitude than had been previously computed owing probably to a lack of variational convergence. For other atomic systems of moderate size it is suggested that the methods of this section can be extended to give computed E_{corr} of the order of the 90% of the true value achieved for the beryllium series. However the non-empirical calculation of correlation energies will not be dealt with further in this work though in Chapter 9 semi-empirical approaches suitable for medium and large atoms will be discussed. Rather the evaluation of other atomic and molecular properties using finite-difference techniques will be described in the next five Chapters commencing with an extensive treatment of the one-centre method in very simple molecules.

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Chapter 4 The Use of Finite-Difference Methods in Single-Centre Molecular Calculations.

4.1 Introduction

The single-centre method has frequently been suggested as a means of calculating the electronic structures of molecules as it eliminates the difficult problem of the evaluation of multicentre integrals. In this Chapter it is investigated with the ultimate objective of developing methods by which the electronic energy of small molecules can be calculated to the same degree of accuracy as the atomic compu--tations carried out in the previous two Chapters. Some progress along these lines has already been made by other workers within the framework of many-body perturbation theory, the treatment of H_2 by Kelly (K9) being a notable example. As here the idea of such a calculation is to extend methods which are appropriate to atoms to simple molecules which of course are not conveniently spherical. Unfortunately only the beginn--ings of the present project can be described as it is necessarily very long-term in nature. Nevertheless it is hoped that the results presented in this section of the thesis, concerning to a large extent the efficacy of the one-centre expansion in determining the energies of simple one-electron molecules, will give a solid foundation on which future progress towards the accurate calculation of molecular structures can be based.

In the first part of this Chapter fairly extensive calcul--ations on the ground and excited states of the hydrogen molecule ion are described using an expansion centre intermediate between the nuclei. As the computations were executed for a wide range of internuclear

distances the extent to which various expansion lengths reproduce the exact potential curves can be properly assessed. Emphasis is also given to the terminal rate of convergence of the one-centre method for diff--eerent states and the efficiency of possible extrapolation procedures for the determination of the contribution of the higher harmonics.

The simplest alternative scheme, namely the use of an expan--sion centre on one of the nuclei, is then examined for the ground state of several systems such as H_2^+, HeH^{++} with again the contribution of successive harmonics being examined for different internuclear distances.

Lastly conditions necessary for the possible successful application of the single-centre method in molecular calculations are briefly discussed together with suggestions of perturbation schemes for incorporating such an approach.

4.2 Theory for the united atom, one-centre expansion for H_2^+

In the united atom* approach the Hamiltonian for H_2^+ can be written as (1).

$$-\tfrac{1}{2}\nabla^2 - 2.0 \times \sum_{k=0}^{\infty} \frac{r_<^{2k}}{r_>^{2k+1}} P_{2k}(\cos\theta) \qquad (1)$$

* This definition of the approach used here as 'united atom' is perhaps a little different from the conventional usage of this term. It is however felt that it is more informative to use such a description rather than an alternative such as 'molecular puff'.

In (1) the quantities $r_<$, $r_>$ are defined as min(r,R), max(r,R), R being half the internuclear distance R_{ab}.

The wavefunction can be expanded in a similar manner.

$$\Phi = r\Psi = \sum_{k=0}^{\infty} f_{2k}(r)\ (4k+1)^{\frac{1}{2}}\ (4\pi)^{-\frac{1}{2}}\ P_{2k}(\cos\theta) \qquad (2)$$

for the σ_g states.

$$\Phi = r\Psi = \sum_{k=0}^{\infty} f_{2k+1}(r)\ (4k+3)^{\frac{1}{2}}\ (4\pi)^{-\frac{1}{2}}\ P_{2k+1}(\cos\theta) \qquad (3)$$

for the σ_u states.

Insertion of (2) into the Schrödinger equation using the Hamiltonian (1) gives rise to an infinite set of coupled differential equations for the $f_{2k}(r)$ of the form (4), entirely analogous expressions being derived for the σ_u states.

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \frac{2k(2k+1)\ r^{-2}}{2} - 2\,M^{2l}(k,k)\right) f_{2k}(r)$$

$$= E\, f_{2k}(r) + 2\sum_{k'\neq k} M^{2l}(k,k')\ f_{2k'}(r) \qquad (4)$$

where

$$M^{2l}(k,k') = \sum_{l} C^{2l}(k,k')\ \frac{r_<^{2l}}{r_>^{2l+1}} \qquad (5)$$

and also

$$C^{2\ell}(k,k') = \tfrac{1}{2}\left((4k+1)(4k'+1)\right)^{\frac{1}{2}} \times \int P_{2k}(\cos\theta)\, P_{2\ell}(\cos\theta)\, P_{2k'}(\cos\theta)\, d(\cos\theta) \qquad (6)$$

For the Π states the situation is a little more complicated but not greatly so, the wavefunction being expnaded in the form (7) or (8).

$$\Phi = r\Psi = \sum_{k=1}^{\infty} f_{2k}(r)\left((4k+1)(2k-1)!\right)^{\frac{1}{2}}\left(4\pi(2k+1)!\right)^{-\frac{1}{2}} \times P^{1}_{2k}(\cos\theta)\exp(i\phi) \qquad (7)$$

for the π_g states.

$$\Phi = r\Psi = \sum_{k=0}^{\infty} f_{2k+1}(r)\left((4k+3)\,2k!\right)^{\frac{1}{2}}\left(4\pi(2k+2)!\right)^{-\frac{1}{2}} \times P^{1}_{2k+1}(\cos\theta)\exp(i\phi) \qquad (8)$$

for the π_u states.

Again this furnishes the set of equations (4) (for the π_g states) with however the $C^{2\ell}(k,k')$ defined as in (9).

$$C^{2\ell}(k,k') = \tfrac{1}{2}\left((4k+1)\,(4k'+1)\,(2k-1)!\;\;(2k'-1)!\;\right)^{\frac{1}{2}}$$
$$\times\;\left((2k+1)!\;\;(2k'+1)!\;\right)^{-\frac{1}{2}}$$
$$\times\int P^{1}_{2k}(\cos\theta)\,P^{1}_{2\ell}(\cos\theta)\,P^{1}_{2k'}(\cos\theta)\,d(\cos\theta) \qquad (9)$$

The corresponding expressions for the π_u states are clearly found by a trivial extension of the above.

As previously stated (4) is an infinite set of coupled differential equations for the $f_{2k}(r)$. They also contain the unknown eigenvalue E which, if the components of the wavefunction have been derived by some process, is given by the summation (10).

$$E = N^{-2}\left(\sum_{\ell}\left(\int f^2_{2k}(r)\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + k(2k+1)r^{-2} - 2\,M^{2\ell}(k,k)\right)dr\right)\right.$$
$$\left.-4\sum_{\ell<\ell'}\sum\left(\int f_{2k}(r)\,M^{2\ell}(k,k')\,f_{2k'}(r)\,dr\right)\right) \qquad (10)$$

where

$$N^2 = \sum_{k}\int f^2_{2k}(r)\,dr \qquad (11)$$

The method which is used to solve accurately for the wavefunction and find E will be described in the next section.

4.3 The solution of the radial equations and the determination of E

Clearly it is impossible to fully solve the equations (4) since an infinite number of terms is involved. However it would seem likely that the inclusion of a reasonable number of harmonics would yield good results as it is obvious that the higher terms in the Hamiltonian (1) are strongly localised at the distance R and at $\theta = 0$ i.e. in the region of the nuclear cusps. For the solution of (4) an iterative approach is necessary with one, two, three ..... terms being successively included, the previous calculation being employed as an initial approximation for the next one. Consider first the equation resulting from the retention of only the first, spherical term:

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} - 2r_>^{-1} \right) f_0(r) = E\, f_0(r) \qquad (12)$$

Now if the exact eigenvalue were known and also an approximation U^0 to $f_0(r)$ then it would be straightforward to find the correction C to U^0 which would give the exact function since:

$$D\,(U^0 + C) = E\,(U^0 + C) \qquad (13)$$

hence

$$(D - E)\,C = (E - D)\,U^0 \qquad (14)$$

Here the eigenvalue is not known and the scheme used is to start with

an initial guess for E, form a correction C^0 to the starting vector and then calculate a hopefully improved eigenvalue from (10). The procedure is continued, with normalisation of the wavefunction after each cycle, until E is constant to the desired degree. Clearly the method will not necessarily converge if a poor approximation to the eigenvalue or the wavefunction is used at the start. In practice, for the particular problems studied, it was found that the scheme converged reliably espe--cially for the lowest state of each symmetry if at all reasonable values were chosen for E^0 and U^0. For excited states a word of comment is apposite as it might be thought that it would be impossible to compute the energy of a requisite state with any certainty.[1] It was though disco--vered that it was not difficult to execute a specific calculation if satisfactory approximations were given initially. For the $f_0(r)$ the main requirement was resolved to be the inclusion at the start of the correct number of nodes. In general the only difficulties that were encountered were for the coupled equations for certain of the excited states at large internuclear distances where coupling between the first and second terms in the wavefunction is very strong. In these cases although for example the correct S limit may be located this is a poor approximation to the D limit energy and thus the process may not con--verge correctly.

Once the one term equation has been solved and the S limit energy determined (so-called as it is the best energy obtainable using only functions of S symmetry) then the D and higher limits can be found

[1] See for example Barraclough and Mooney (B3) for a discussion of this question with approriate references.

by extension of the above method. The only difference is the presence of the coupling terms in the inhomogeneity for each equation but this does not cause any particular difficulty. Neither does the computat--ional labour rise very much for each limit as the effect on the f_{2k} of adding another harmonic is small after the first two or three terms.

As far as the solution of the equations of the type (14) is concerned techniques rather similar to those used for the Illustrative Example 1.2 were utilised:

A simple three-point difference formula was taken for the second derivative and the resulting tridiagonal matrix equations were solved on a series of 'square root' grids containing from about 100 to 500 strips. The eigenvalues were extrapolated using the Richardson process to give at least 6 to 7 figure accuracy. An important technicall point concerning the extrapolation process is the necessity to arrange the grid sizes and radial cutoffs such that a grid point always occurs at the distance R i.e. at the nuclei. Otherwise rather erratic results are recorded if it is attempted to obtain extreme accuracy although it is still possible to obtain about five figures reliably (about the same as is found in variational treatments of this type of problem) if grids containing relatively few strips are used.

4.4 Results for the σ states of H_2^+

For several σ states of H_2^+ the eigenenergies for the various limits have been calculated at a wide range of internuclear distances. The convergence and other properties of the single-centre expansion will now be examined, first for the ground state and then for the excited states.

A The ground state ..... $1s\sigma_g$

The eigenvalues for expansion lengths up to five terms are given in Table 4.1 for the ground state. Additionally in some cases harmonics up to $\ell = 12$ have been included. From Table 4.2 it can be seen that the present results agree well with previous calculations which have virtually been confined to the equilibrium internuclear distance of 2.0 a.u.. Of particular interest are the S limit computations as this problem is capable of exact solution as has been carried out by Hauk and Parr (H5). Over a wide range of R_{ab} it is found that the discrepancy between the latter's values and those displayed in Table 4.1 is no more than 1 part in 10^6 and is frequently less.

The behaviour of the limiting energies with variation of R_{ab} is much as one might expect. For short internuclear distances these are in harmony with the exact eigenvalues of Wind (W11) with for example the error in the O limit energy for $R_{ab} = 0.5$ a.u. being only 1 in 50 000. Indeed the spherical term is dominant reflecting the approach of the molecular wavefunction to that of the united atom. However as the inter--nuclear distance increases the differences between the exact values and those from the one-centre expansion rise sharply showing the need for more terms in the calculation. This bias towards the shorter R_{ab} is also observed in the computed equilibrium bondlength for the molecule. As can be seen from Figure 4.1 as successive harmonics are added to the expan--sion it increases from too short a distance to the correct value of 2.0 a.u. for the I and K limits. Before leaving this question it may be commented that this distortion of the potential curve is perhaps the weakest point of the single-centre approach since an approximation which runs parallel to the true curve is often of more practical use than one which varies in accuracy over a range of internuclear distances.

Table 4.1 The eigenvalues for the $1s\,\sigma_g$ state for H_2^+.

R_{ab}	S Limit	D Limit	G Limit	I Limit	K Limit	M Limit	O Limit
0.5	-1.716567	-1.733113	-1.734493	-1.734792	-1.734892	-1.734934	-1.734955
1.0	-1.406144	-1.445263	-1.449935	-1.451032	-1.451409	-1.451569	-1.451650
1.5	-1.181937	-1.236674	-1.245240	-1.247420	-1.248195	-1.248526	-1.248695
1.6	-1.145193	-1.202360	-1.211744	-1.214173	-1.215041	-	-
1.7	-1.110650	-1.170060	-1.180273	-1.182960	-1.183938	-	-
1.8	-1.078127	-1.139611	-1.150662	-1.153619	-1.154691	-	-
1.9	-1.047461	-1.110863	-1.122762	-1.126000	-1.127181	-	-
2.0	-1.018503	-1.083681	-1.096438	-1.099967	-1.101264	-1.101825	-1.102112
2.1	-0.991118	-1.057943	-1.071566	-1.075399	-1.076818	-	-
2.2	-0.965185	-1.033539	-1.048036	-1.052184	-1.053731	-	-
2.3	-0.940593	-1.010368	-1.025747	-1.030222	-1.031904	-	-
2.4	-0.917243	-0.988340	-1.004607	-1.009422	-1.011246	-	-
2.5	-0.895044	-0.967371	-0.984534	-0.989702	-0.991674	-0.992537	-0.992984
3.0	-0.798674	-0.876016	-0.897750	-0.904872	-0.907702	-0.908956	-0.909616
3.5	-0.721382	-0.802292	-0.828695	-0.838099	-0.841997	-0.843766	-0.844689
5.0	-0.560166	-0.646637	-0.686782	-0.704680	-0.713126	-0.717134	-0.719382

Table 4.2 A comparison of results for the 1s σ_g state for H_2^+ at the internuclear distance of 2.0 a.u.

	Present calculation	Joy & Handler[a]	Cohen & Coulson[b]	Hauk & Parr[c]	Winter & McKoy[d]
S Limit	-1.018502_7	-1.018501	-1.01851	-1.0185023	-1.018507
D Limit	-1.083681	-1.083674	-	-	-
G Limit	-1.096438	-1.096404	-	-	-
I Limit	-1.099967	-1.099919	-1.09994	-	-
K Limit	-1.101264	-1.101214	-	-	-

[a] Reference (J2)

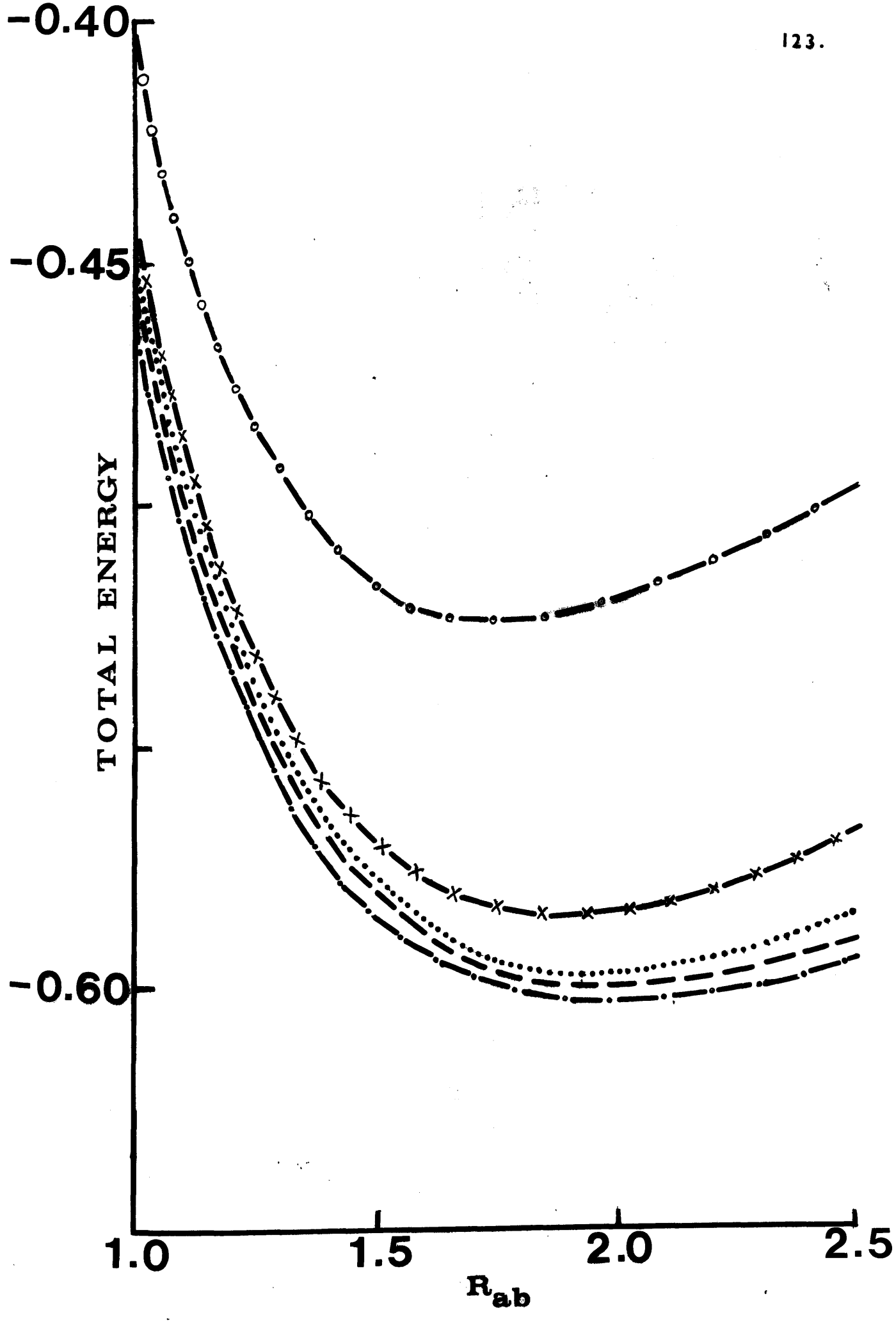
[b] Reference (C10)

[c] Reference (H5)

[d] Reference (W16)

Figure 4.1

The total ground state energy of H_2^+ for the successive limits:- S limit — O — O — ; D limit — X — X — ; G limit ..... ; I limit — — — — ; K limit — . — . — ;


-0.40
-0.45
-0.60
TOTAL ENERGY
1.0
1.5
2.0
2.5
R_{ab}

The trend in the convergence of the expansion with the addition of terms is most interesting. Hayes and Parr (H6) have demonstr-ated for a very limited number of internuclear distances that, in the limit of high ℓ, the increment to the energy from the inclusion of another harmonic in the series is proportional to ℓ^{-4}. This is corrobo-rated by Figure 4.2 in which $\log(|\Delta E_\ell|)$ has been plotted versus $\log(\ell)$ for R_{ab} = 0.5, 1.0 and 2.0 a.u., ΔE_ℓ being the appropriate energy increment. The first of these is almost linear with the expected limiting gradient of -4 but as R_{ab} increases the graph displays more curvature. This is also seen in Table 4.3 where extrapolants from 5,6 and 7 term exp-ansions, calculated on the assumption of the above asymptotic behaviour, are given. Clearly the procedure appears satisfactory for the short and medium internuclear distances but breaks down for the larger values of R_{ab}. Nonetheless even at 5.0 a.u. it may be noted that the error in the 0 limit extrapolant is less than 1 Kcal, a point which will be returned to later when the possible extension to other systems will be considered.

B <u>The excited states</u> ..... $2p\,\sigma_u$, $3p\,\sigma_u$, $4p\,\sigma_u$, $2s\,\sigma_g$, $3s\,\sigma_g$, $4f\,\sigma_u$, $3d\,\sigma_g$.

In Table 4.4 eigenvalues, extrapolants and exact results are compared for the $2p\,\sigma_u$ state for a selection of internuclear dist-ances as for the ground state. Similar calculations have been executed for the other excited states but space precludes an extensive listing of the energies of these states here. However for the ground state equilibrium distance of 2.0 a.u., for which exact results are readily available, these quantities are collected in Tables 4.5 and 4.6.

For the $2p\,\sigma_u$ state the convergence rate and other properties

Figure 4.2

Log($| \Delta E_{\ell} |$) versus log(ℓ) for the $1s\,\sigma_g$ state of H_2^+ for R_{ab} = 0.5, 1.0 and 2.0 a.u. (A, B and C respectively). The asymptotic gradient of -4 is shown in each case.

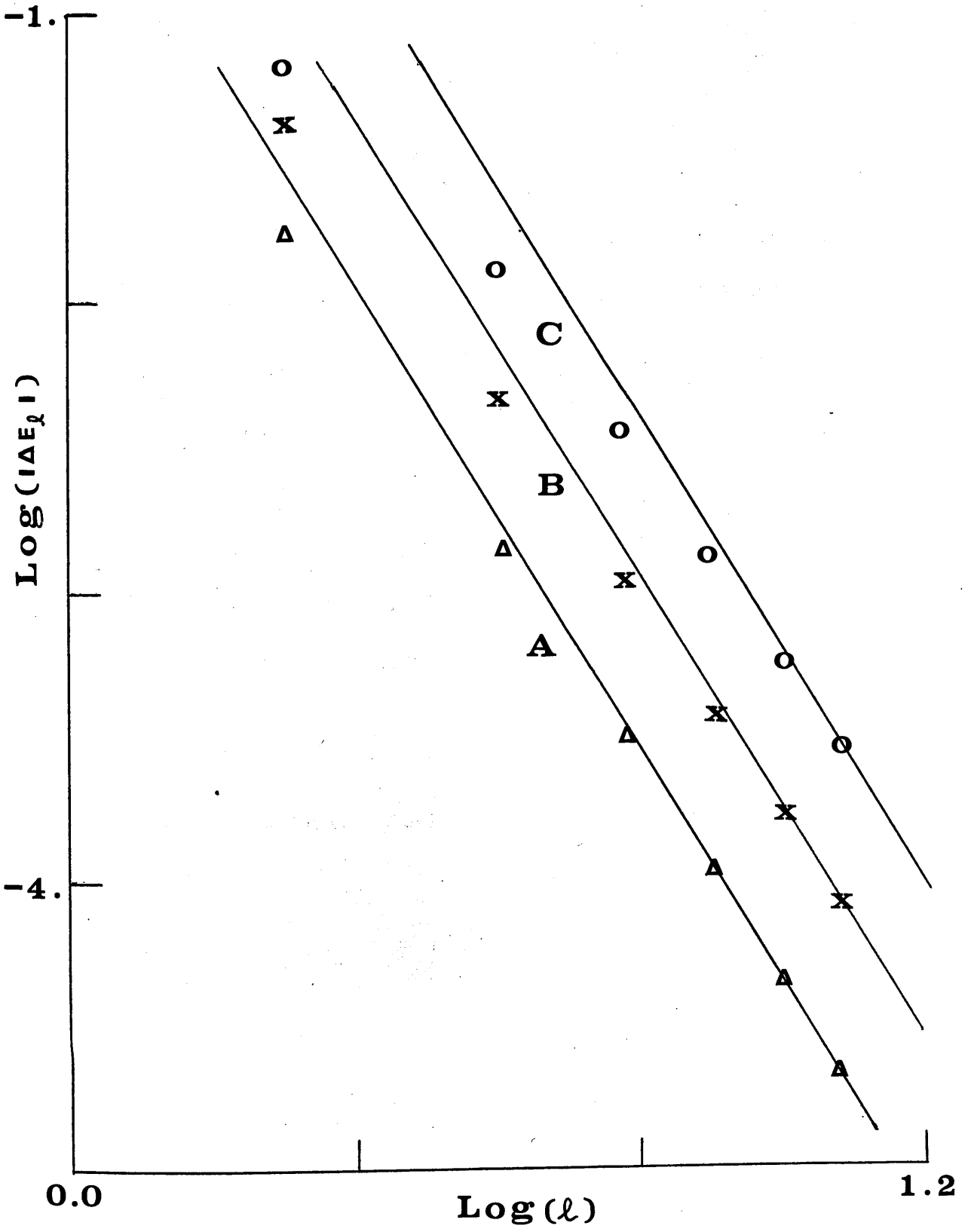

-1.
-4.
Log(|ΔE_ℓ|)
0.0
1.2
Log(ℓ)
A
B
C

Table 4.3 A comparison of the extrapolants from 5, 6 and 7 term expansions for the $1s\sigma_g$ state of H_2^+ and the exact eigenvalues of Wind (W11).

R_{ab}	K Limit[a]	M Limit	O Limit	Exact
0.5	-1.73498	-1.73499	-1.73499	-1.73499
1.0	-1.45175	-1.45177	-1.45178	-1.45179
1.5	-1.24890	-1.24893	-1.24896	-1.24899
2.0	-1.10245	-1.10252	-1.10256	-1.10263
2.5	-0.99348	-0.99360	-0.99368	-0.99382
3.0	-0.91029	-0.91050	-0.91064	-0.91090
3.5	-0.84556	-0.84595	-0.84612	-0.84657
5.0	-0.72085	-0.72208	-0.72288	-0.72442

[a] Extrapolant from K limit. Similarly for the next two columns.

Table 4.4 The eigenvalues and L limit extrapolant for the $2p\sigma_u$ state of H_2^+.

R_{ab}	P Limit	F Limit	H Limit	J Limit	L Limit	Extrapolant	Exact[a]
0.5	-0.516496	-0.516855	-0.516877	-0.516882	-0.516884	-0.51589	-0.51589
1.0	-0.558420	-0.563946	-0.564542	-0.564694	-0.564751	-0.56481	-0.56481
1.2	-0.576376	-0.586681	-0.587984	-0.588328	-0.588457	-0.58860	-0.58861
1.4	-0.592075	-0.608528	-0.610903	-0.611552	-0.611799	-0.61206	-0.61208
1.6	-0.604414	-0.627867	-0.631658	-0.632730	-0.733142	-0.63358	-0.63361
1.8	-0.613019	-0.643788	-0.649278	-0.650879	-0.651504	-0.65217	-0.65223
2.0	-0.618011	-0.656006	-0.663398	-0.665620	-0.666499	-0.66744	-0.66754
2.5	-0.617536	-0.671701	-0.684313	-0.688386	-0.690051	-0.69184	-0.69207
3.0	-0.604592	-0.671370	-0.689318	-0.695518	-0.698137	-0.70095	-0.70143
3.5	-0.585078	-0.661173	-0.684224	-0.692707	-0.696411	-0.70038	-0.70121
4.0	-0.562648	-0.645445	-0.673224	-0.684077	-0.688977	-0.69423	-0.69555
4.5	-0.539377	-0.626896	-0.658986	-0.672249	-0.678439	-0.68508	-0.68705
5.0	-0.516390	-0.607154	-0.643132	-0.658809	-0.666368	-0.67447	-0.67729

[a] Taken from references (B6) and (B7).

Table 4.5 S to K limits for the electronic energy for the $2s\,\sigma_g$, $3s\,\sigma_g$, $3d\,\sigma_g$ states of H_2^+ at the ground state equilibrium distance of 2.0 a.u..

	$2s\,\sigma$	$3s\,\sigma$	$3d\,\sigma$
S limit	-0.350344	-0.174448	—
D limit	-0.358447	-0.176915	-0.234430
G limit	-0.360049	-0.177422	-0.235640
I limit	-0.360510	-0.177568	-0.235735
K limit	-0.360682	-0.177623	-0.235758
Extrapolant	-0.360839	-0.177673	-0.235779
Exact (B6)	-0.36086_5	-0.17768	-0.23577_5

Table 4.6 P to L limits for the electronic energy for the 3p σ_u, 4p σ_u, 4f σ_u states of H_2^+ at the ground state equilibrium distance of 2.0 a.u..

	3pσ	4pσ	4fσ
P limit	-0.245923	-0.133739	—
F limit	-0.253167	-0.136463	-0.126601
H limit	-0.254603	-0.137006	-0.126644
J limit	-0.255038	-0.137171	-0.126644
L limit	-0.255210	-0.137236	-0.126644
Extrapolant	-0.255394	-0.137306	-0.126644
Exact (B6)	-0.25541_5	-0.13731_5	-0.12664_5

are remarkably similar to those for the ground state previously discussed. Again the l^{-4} terminal rate is found and, as can be observed from the Table, while the extrapolation process gives excellent results for R_{ab} less than about 3.0 a.u. for greater internuclear distances it is not reliable.

For the other states convergence is perceptibly faster though a limiting rate proportional to l^{-4} is still apparently maintained, the only possible exceptions being interestingly 3d σ_g and 4f σ_u for which convergence is very rapid and it is not possible to assess such a prop--erty with any degree of certainty. Indeed for the 3s σ_g, 3d σ_g, 4p σ_u and 4f σ_u states the extrapolants even for the five term wavefunctions used here are within the error limits on the exact results of Bates, Ledsham and Stewart (B6).* The faster convergence rate is as might be exp--ected since the greater radial extension of the wavefunctions makes for example the one term, spherical, approximation for the ns σ_g states more reasonable. An additional, but related, factor is probably a relative decline in the importance of the singularity at each nucleus. As can be seen from Figure 4.3, and as been previously discussed by Cohen and Coulson (C10), for the ground state after the first two or three additio--nal harmonics only really contribute to the wavefunction near the nuclei. For the excited states this effect would still be expected to occur but

* Since the original preparation of this part of the manuscript some extremely accurate results have been communicated to me by Dr. James D. Power of the National Research Council of Canada. A comparison of the more accurate of the single-centre calculations and this new data is given briefly in the Addenda and Corrigenda at the end of this work.

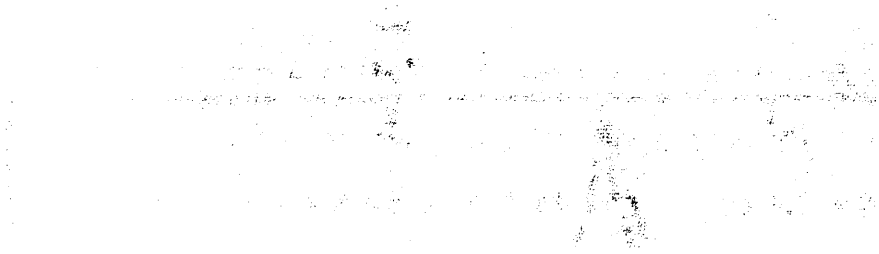
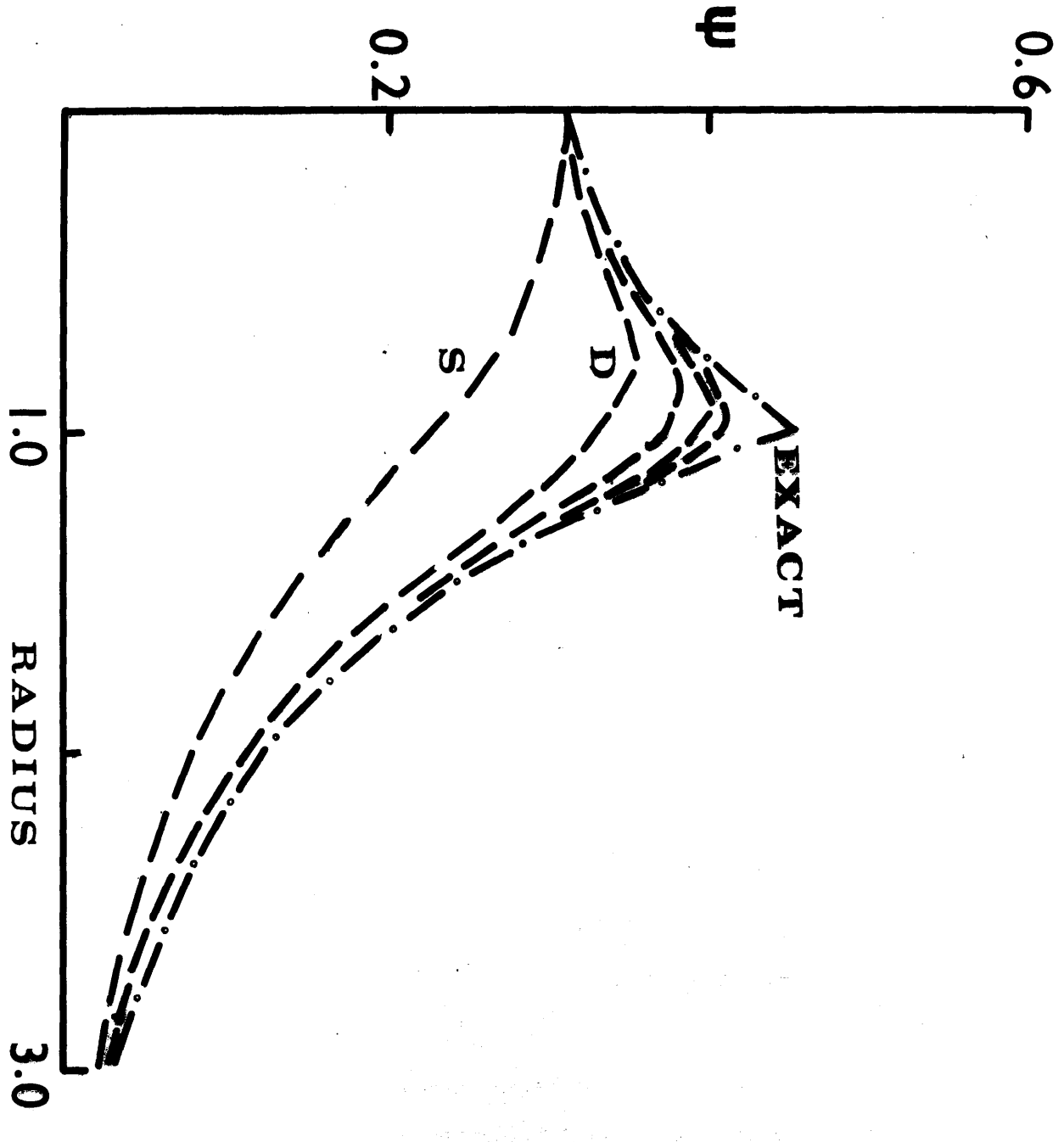


Figure 4.3

The values of the exact wavefunction and the S to K limit approximations for the ground state of H_2^+ along the internuclear axis at the equilibrium R_{ab} of 2.0 a.u..


ψ
0.2
0.6
1.0
3.0
RADIUS
S
D
EXACT

probably be of lesser energetic importance in harmony with the computa-tions.

Thus the one-centre scheme used here is generally more successful for the excited states than for the ground state with for $R_{ab} < 2.0$ a.u. comparable accuracy to that obtainable by conventional techniques. However for large internuclear distances, even with expansions longer than five terms, the results would still leave something to be desired e.g. the reproduction of the known shallow minimum in the $3d\,\sigma_g$ potential curve appears completely impractical within a single-centre framework.

4.5 Results for the π states of H_2^+ ..... $2p\,\pi_u$, $3p\,\pi_u$, $3d\,\pi_g$, $4d\,\pi_g$

In the preceding section for the σ states it was found that it was only possible to approach the exact eigenenergy at smaller values of the internuclear distance with an extrapolation procedure being necess-ary to give high accuracy. However calculations by Cohen (C9) and Hoyland (H8) suggest that for π states the single-centre method should be capable of giving satisfactory results even at large R_{ab}. In order to verify this point computations were performed for several π states of the hydrogen molecule ion with expansion lengths of up to seven terms. In Tables 4.7 and 4.8 total energies for the $2p\,\pi_u$ and $3d\,\pi_g$ states are reported at a representative selection of internuclear distances together with the most accurate values of the exact energy available to the author. Also included are limiting estimates of the energy obtained by extrapolation as descr-ibed below.

Table 4.7 Total energies i.e. electronic energy plus R_{ab}^{-1} for the $2p\,\pi_u$ state of H_2^+.

R_{ab}	2.0	4.0	6.0
P limit	0.07425721	-0.09235259	-0.11733530
F limit	0.07139074	-0.09984565	-0.12789890
H limit	0.07125099	-0.10064657	-0.12977012
J limit	0.07123378	-0.10077662	-0.13015987
L limit	0.07123006	-0.10080775	-0.13026402
N limit	0.07122895	-0.10081753	-0.13029858
P' limit	0.07122854	-0.10082124	-0.13031209
Extrapolant	0.07122818	-0.10082448	-0.13032391
Exact[a]	0.0712281801	-0.1008246441	-0.1303248957

R_{ab}	8.0	10.0
P limit	-0.11754955	-0.11181416
F limit	-0.13000368	-0.12542245
H limit	-0.13323656	-0.13021527
J limit	-0.13408954	-0.13179307
L limit	-0.13434666	-0.13233413
N limit	-0.13443752	-0.13253971
P' limit	-0.13447438	-0.13262676
Extrapolant	-0.13450662	-0.13270289
Exact[a]	-0.1345106313	-0.1327162901

[a] Private communication, reference (P6).

Table 4.8 The total energies for the 3d π_g state of H_2^+.

R_{ab}	2.0	4.0	6.0
D limit	0.27385380	0.02411733	-0.04870504
G limit	0.27331764	0.01954309	-0.05879413
I limit	0.27330268	0.01913861	-0.06038399
K limit	0.27330096	0.01907281	-0.06071843
M limit	0.27330058	0.01905627	-0.06081240
O limit	0.27330046	0.01905082	-0.06084521
Q limit	0.27330042	0.01904867	-0.06085861
Extrapolant	0.27330038	0.01904658	-0.06087162
Exact[a]	0.2733003734	0.0190465577	-0.0608722224

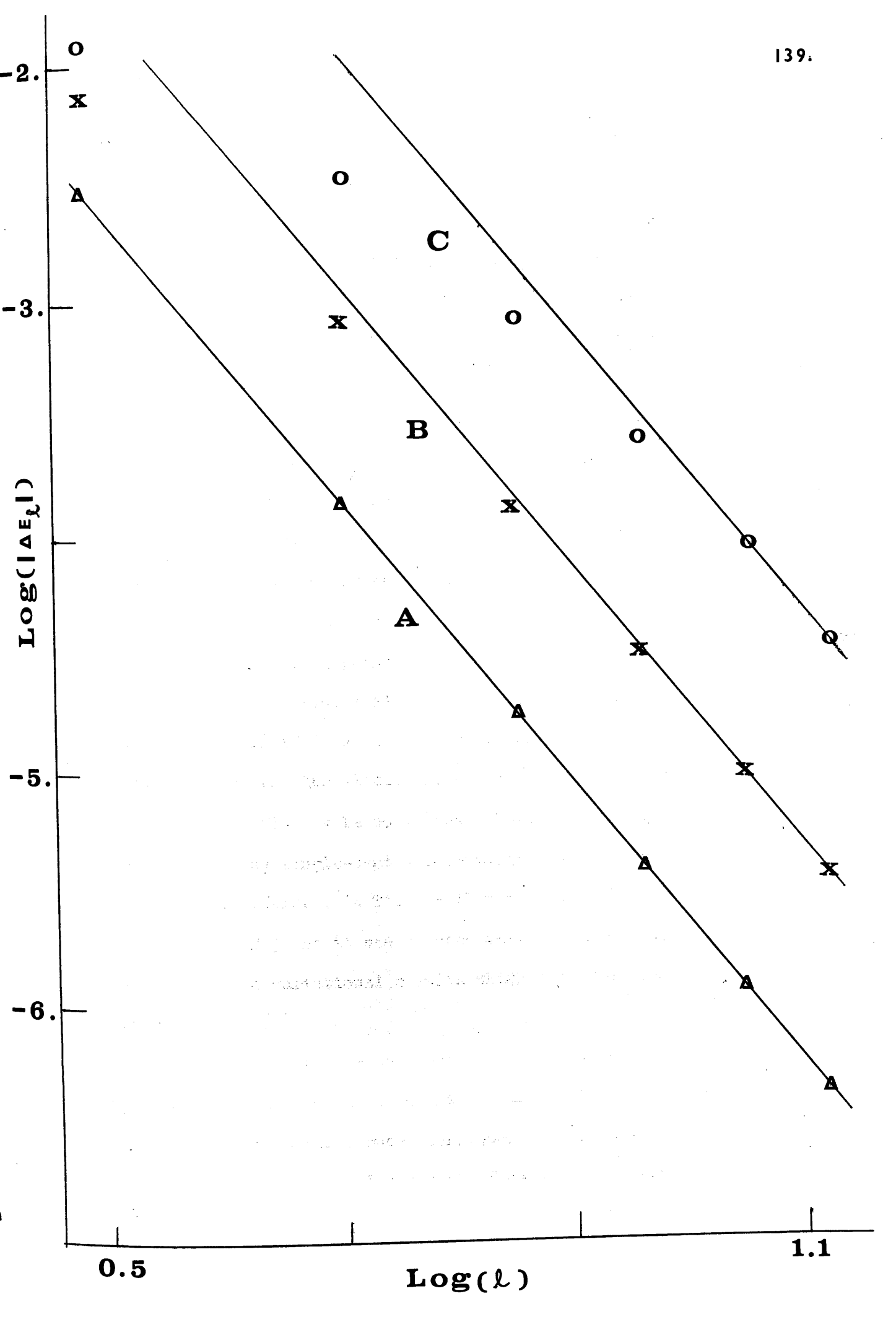
R_{ab}	8.0	10.0
D limit	-0.07546261	-0.08517930
G limit	-0.08981828	-0.10229123
I limit	-0.09308847	-0.10735982
K limit	-0.09393996	-0.10894470
M limit	-0.09420673	-0.10949743
O limit	-0.09430554	-0.10971534
Q limit	-0.09434736	-0.10981120
Extrapolant	-0.09438793	-0.10990419
Exact[a]	-0.0943915183	-0.1099168745

Probably the most interesting feature of these calculations is the rate of convergence of the eigenvalue to the exact energy as the number of terms in the expansion is increased. It is very noticeable that in this case the convergence is much superior to that for the σ states for which the terminal rate ℓ^{-4} was found previously. In Figure 4.4, for the $2p\,\pi_u$ state at a number of internuclear distances, $\log(|\Delta E_\ell|)$ is plotted versus $\log(\ell)$, entirely similar graphs being obtained for the other states which were examined. It is evident that for these states in the limit of high ℓ the energy increments go as ℓ^{-6}. A very interesting, though speculative, analogy can be drawn between this result and the con-vergence rate for the partial wave contributions to $\varepsilon 2$ for electron pair functions discussed in Chapters 2 and 3. For the latter limiting rates proportional to ℓ^{-4} and ℓ^{-6} were found for the space symmetric and antisymmetric pairs respectively, the slow convergence for the symmetric case being attributed to the singularity in the electron interaction term. Similarly it seems reasonable that the ℓ^{-4} rate for the σ states is consequent on the difficulties associated with representing the cusp at the nuclei sinc, as was seen before in Figure 4.3 for the ground state, the later harmonics only contribute significantly near the nuclei. Hence for states nodal in this region improved convergence is expected. It would thus appear that the proposal of Hayes and Parr (H6) that the limit-ing rate is some function of m is unlikely, certainly not $\propto \ell^{-(4+m)}$ as they very tentatively suggest.

In Tables 4.7 and 4.8 values of the energy are estimated extr-apolating on the basis of the proposed ℓ^{-6} convergence. As can be obse-rved the accuracy of the results is very encouraging with the finding of a shallow minimum in the energy for the $2p\pi_u$ state at 8.0 a.u. whereas the $3d\,\pi_g$ state is correctly repulsive over the whole range. With

Figure 4.4

Log($|\Delta E_\ell|$) versus log(ℓ) for the $2p\pi_u$ state of H_2^+ for R_{ab} = 2.0, 4.0 and 8.0 a.u. (A, B and C respectively) with the proposed limiting gradient of -6 shown in each case.


-2.
-3.
-5.
-6.
Log(|ΔE_ℓ|)
0.5
1.1
Log(ℓ)
A
B
C

extrapolation it is found that only perhaps at 10.0 a.u. are the present calculations deficient, insufficient terms having been included to reach the terminal rate of convergence. It can be noted that for shorter inter--nuclear distances very high accuracy is achieved with excellent agree--ment between the exact values and the present results to the precision given in the Tables. Indeed for small R_{ab} no extrapolation is required to give such a degree of accuracy. This is illustrated by results for the $3d\,\pi_g$ state for which at 1.5 a.u. the Q limit agrees with the exact energy to 8 digits while by 1.0 a.u. only a five harmonic expansion (M limit) is required to recover such accuracy.

For the other states considered similar accuracy is believed to be maintained with convergence of the eigenenergies and extrapolants from above. In Tables 4.9 and 4.10 some results are listed for the $3p\,\pi_u$ and $4d\,\pi_g$ states and it is perhaps sufficient to observe that for example the $3p\,\pi_u$ state at 5.0 a.u. a P' limit of -0.16517727 a.u. and an extrapolant of -0.16517954 a.u. compare gratifyingly with the value of Wallis and Hulbert for the electronic energy of -0.16517970 a.u. (W1).*

It may finally be noted that these calculations are in harmony with the few single-centre computations on π states which have been previously performed. In Table 4.11 this work is compared with the study of Hoyland (H8) and it can be seen that the numerical values fall uniformly below the variational results which are of course upper bounds to each limit.

Overall it can be concluded that for these states the single-centre, united atom approach gives remarkably accurate results especially when finite-difference techniques are employed for the calcul--ation. Even at 10.0 a.u. a discrepancy of only about 1 part in 10 000

* See Addendum for a comparison with very accurate data recently received.

Table 4.9 The electronic energies for the P to P' limits for the $3p\pi_u$ state of H_2^+ at R_{ab} = 1.5 and 5.0 a.u..

R_{ab}	1.5	5.0
P limit	-0.20736195	-0.16228883
F limit	-0.20784694	-0.16470850
H limit	-0.20786712	-0.16507221
J limit	-0.20786949	-0.16514794
L limit	-0.20786999	-0.16516805
N limit	-0.20787014	-0.16517468
P' limit	-0.20787020	-0.16517727
Extrapolant	-0.20787025	-0.16517954
Exact	-0.207870[a]	-0.16517970[b]

[a] Reference (B7).

[b] Reference (W1).

Table 4.10 The electronic energies for the D to Q limits for the $4d\,\pi_g$ state of H_2^+ at R_{ab} = 1.5 and 6.0 a.u..

R_{ab}	1.5	6.0
D limit	-0.12602928	-0.12026728
G limit	-0.12611413	-0.12352044
I limit	-0.12611579	-0.12409052
K limit	-0.12611596	-0.12422086
M limit	-0.12611600	-0.12425877
O limit	-0.12611601	-0.12427223
Q limit	-0.12611601	-0.12427777
Extrapolant	-0.12611601	-0.12428341
Exact (B7)	-0.126116	-0.124283

Table 4.11 A comparison of the present results and those of Hoyland (H8) at the internuclear distance of 8.0 a.u. for the $2p\pi_u$ state of H_2^+.

	Hoyland	This work	Difference
P limit	-0.117549	-0.11754955	-0.000001
F limit	-0.130001	-0.13000368	-0.000003
H limit	-0.133234	-0.13323656	-0.000003
J limit	-0.134085	-0.13408954	-0.000005
L limit	-0.134341	-0.13434666	-0.000006
N limit	-0.134431	-0.13443752	-0.000007
P' limit	-0.134467	-0.13447438	-0.000007
Extrapolant	-0.134508*		

* Obtained by graphical extrapolation process.

in the electronic energy is obtained and it would appear that the method is competitive with conventional procedures over a wide range of inter--nuclear distances, a result of some interest since, as remarked by Bhatia and Temkin (B8), a one-centre approach can considerably simplify certain problems such as are found in scattering calculations.

4.6 Alternative single-centre scheme: expansion centre on one nucleus

In the previous sections single-centre calculations have been described for the hydrogen molecule ion in which an expansion centre intermediate between the nuclei was used. However for more general systems e.g. heteronuclear diatomics this choice of origin is not appropriate and an alternative scheme has to be employed. In this part of the work studies of one-electron diatomic molecules using the simpl--est possibility viz, that of an expansion centre on one of the nuclei will be discussed.* As before simple finite-difference methods are utilised to give computations of high accuracy.

A Theory

Consider a one-electron diatomic system with charges Z_a and Z_b on the nuclei which are separated by R a.u.. Using nucleus a as the origin the Hamiltonian can be expressed as (15):-

* This is certainly not the only computationally feasible alternative. See for example Rabinovich and Hauk, Kim, Parr and Hameka references (R1, H4).

$$-\tfrac{1}{2}\nabla^2 - Z_a/r - Z_b \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\theta) \qquad (15)$$

As for the previous calculations the wavefunction can be written as an expansion in Legendre polynomials (16) with the f_k to be determined from the coupled equations (17).

$$\Phi = r\Psi = \sum_{k=0}^{\infty} f_k(r)\,(2k+1)^{\frac{1}{2}}\,(4\pi)^{-\frac{1}{2}}\,P_k(\cos\theta) \qquad (16)$$

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}k(k+1)r^{-2} - Z_a r^{-1} - M^{\ell}(k,k)\right) f_k(r)$$

$$= E f_k(r) + \sum_{k' \neq k} M^{\ell}(k,k')\, f_{k'}(r) \qquad (17)$$

where

$$M^{\ell}(k,k') = Z_b \sum_{\ell} C^{\ell}(k,k') \frac{r_<^{\ell}}{r_>^{\ell+1}} \qquad (18)$$

with

$$C^{\ell}(k,k') = \tfrac{1}{2}\left((2k+1)(2k'+1)\right)^{\frac{1}{2}} \int P_k(\cos\theta)\, P_{\ell}(\cos\theta) \times P_{k'}(\cos\theta)\, d(\cos\theta) \qquad (19)$$

It is obviously observed that the equations (17) are scarcely different from (4) which have been dealt with already. The principal distinction between the two sets of differential equations is the necessity to

include both even and odd k due to the dissymmetry in the nuclear terms in (15) this having, as will be seen, a substantial effect on the rate of convergence of the expansion to the exact energy. Despite this the similarity of (17) to (4) is such that the numerical techniques descri--bed in section 4.3 could be used without amendment to solve for the f_k with results as detailed below.

B Off-centre hydrogen atom

The choice $Z_a = 0$ and $Z_b = 1$ constitutes a particularly sensitive test of the accuracy of the methods used in this section. The exact solution of the infinite set of coupled equations (17) must of course correspond to the hydrogen atom 1s orbital with eigenvalue -0.5 a.u. and thus it is a convenient system on which to examine the efficiency of the present one-centre approach.

In Table 4.12 the various limits are listed for the off--centre hydrogen atom for $R_{ab} = 0.1$, 0.2, 0.5 and 1.0 a.u. together with extrapolated values of the energy obtained assuming an ℓ^{-4} convergence rule as for H_2^+. Such a terminal rate has already been suggested by Hayes and Parr (H6) (although their definition of the energy increment ΔE_ℓ is somewhat different from that used in this work*) and it may be conf--irmed by the usual log./log. plot. Clearly the convergence is much less

* Similarly Hayes and Parr's energies for each are not the same as the S, P ..... limits used here. Their energy for example for $\ell = 0$ represents the contribution of the spherical part of say a 23 harmonic wavefunction to the energy rather than the solution of (17) using only one term in the wavefunction.

Table 4.12 The eigenvalues for the off-centre hydrogen atom problem at a selection of R_{ab}.

R_{ab}	0.1	0.2
S limit	-0.494408	-0.481351
P limit	-0.499752	-0.498328
D limit	-0.499952	-0.499629
F limit	-0.499983	-0.499861
G limit	-0.499992	-0.499932
H limit	-0.499996	-0.499962
I limit	-0.499998	-0.499977
Extrapolant	-0.500001*	-0.500000

R_{ab}	0.5	1.0
S limit	-0.429143	-0.351536
P limit	-0.484243	-0.440786
D limit	-0.495236	-0.474703
F limit	-0.498037	-0.487736
G limit	-0.499009	-0.493299
H limit	-0.499431	-0.495978
I limit	-0.499643	-0.497407
Extrapolant	-0.499973	-0.499629

* Marginal error due to expected inaccuracy in numerical procedures of about 1 part per million.

satisfactory than for the H_2^+ computations, this being attributable to two causes:-

1/ The relatively greater distance of the expansion centre from the centre of electronic charge.

2/ The need to include all harmonics, both even and odd, with the result that it becomes impractical to include those with very high ℓ which are probably necessary to give a reasonable representation of the cusp at b.

Even with extrapolation for a value of R_{ab} greater than 1.0 a.u. the error in the energy is 1 part in 1000 or more as can be seen from Table 4.13. In the latter the % of the discrepancy between the I limit and the exact eigenvalue recovered by the extrapolation process is also listed and the gradual breakdown in the assumption of ℓ^{-4} convergence for $\ell \geqslant 6$ is noticeable as R_{ab} increases. It is apposite though to remark that the extrapolation process is much more efficient in removing this discrepancy than was found by Hayes and Parr in their variational study. In general they found a residual error at least as large as the extrapolated increment with for example for R_{ab} = 0.6 a.u., using an 11 term expansion, these authors obtaining an energy of -0.49961 a.u. giving -0.49975 a.u.. In contrast the present results for a seven harmonic function furnish an energy and extrapolant of -0.49939 and -0.49995 a.u. illustrating the need to use very accurate methods if high precision is required, the deficiency in the variational studies being a consequence of cumulative error due to the necessary truncation of the radial expansions of the f_k.

To conclude this subsection it can be said that although convergence is rather slow for this type of single-centre scheme it does seem capable of yielding results of high accuracy under suitable

Table 4.13 S, I limits and extrapolants for the off-centre hydrogen atom. In the final column the percentage of the discrepancy between the I limit and the exact eigenvalue of -0.5 a.u. eliminated by the extrapolation process is noted.

R_{ab}	S limit	I limit	Extrapolant	% recovered
0.1	-0.494408	-0.499998	-0.500001	——
0.2	-0.481351	-0.499977	-0.500000	100.
0.3	-0.464804	-0.499922	-0.499997	96.
0.4	-0.447005	-0.499815	-0.499989	94.
0.5	-0.429143	-0.499643	-0.499973	92.
0.6	-0.411821	-0.499394	-0.499948	91.
1.0	-0.351536	-0.497407	-0.499629	86.
1.4	-0.305270	-0.493540	-0.498667	79.
1.8	-0.269532	-0.487695	-0.496654	73.

circumstances. These will be investigated in the following paragraphs.

C The hydrogen molecule ion

If the above calculations on the off-centre hydrogen atom could be carried through so as to include an infinite number of harmonics the resulting wavefunction would possess spherical symmetry about the nuclear centre. This is however not the case and the above system has a non-zero dipole moment when this is evaluated from a single-centre wavefunction which necessarily is truncated. It is thus of considerable interest to examine the convergence of the one-centre expansion for the homonuclear H_2^+ system when one of the nuclei is used as the expansion centre and hence the resulting wavefunction cannot fully reflect the symmetry of the molecule.

In Table 4.14 are listed S to I limits and ℓ^{-4} extrap--olants for the electronic energy of H_2^+ together with exact values of the energy. At first sight the properties of the single-centre expansion appear very similar to those for the united atom type previously discussed but with a considerably slower rate of convergence. Closer examination however reveals a substantial qualitative difference between the two sets of calculations. If one considers the S limit energy as a percentage of the exact energy for the non-symmetrical computations this is 93%, 87% and 97% at R_{ab} = 0.5, 2.0 and 5.0 a.u. in contrast to the united atom model for which the corresponding quantity diminishes monotonically. This effect is understandable when the dissociation limits for the two approaches are noted: for the united atom method the spherical limit gives dissociation into two protons and a free electron whereas the other choice of expansion centre yields the lower energy aggregate of a hydrogen atom plus a proton. The result of this, as has been pointed

Table 4.14 S to I limits for the electronic energy of H_2^+ using an expansion centre on one nucleus.

R_{ab}	0.5	1.0	1.5	1.8
S limit	-1.610493	-1.295580	-1.103351	-1.022427
P limit	-1.702155	-1.387540	-1.173595	-1.079640
D limit	-1.723622	-1.422218	-1.207221	-1.109722
F limit	-1.730000	-1.436647	-1.224702	-1.127136
G limit	-1.732399	-1.443238	-1.234101	-1.137366
H limit	-1.733480	-1.446555	-1.239379	-1.143498
I limit	-1.734035	-1.448373	-1.242492	-1.147288
Extrapolant	-1.73490	-1.45120	-1.24733	-1.15318
Exact (W11)	-1.73499	-1.45179	-1.24899	-1.15581

R_{ab}	2.0	2.2	2.5
S limit	-0.978228	-0.940148	-0.892199
P limit	-1.027556	-0.982359	-0.925223
D limit	-1.054761	-1.006514	-0.944797
F limit	-1.071559	-1.022346	-0.958700
G limit	-1.082004	-1.032752	-0.968612
H limit	-1.088546	-1.039565	-0.975559
I limit	-1.092721	-1.044062	-0.980393
Extrapolant	-1.09921	—	—
Exact (W11)	-1.10263	-1.05539	-0.99382

by Katriel (K5) in his study of such shape restricted wavefunctions in the hydrogen molecule ion, is that the spherical limit for H_2^+ is not σ_g in type for longer internuclear distances. The differences in the approaches perhaps becomes more transparent on comparing the total energy curves for the two models, in Figure 4.5 total energies being plotted for the present set of calculations. In contrast to the sit--uation for the united atom ground state calculation, for which all limits give a minimum in the potential curve, the S limit curve is repulsive with the higher harmonics being required to give binding. Consequently the 1 term wavefunction interestingly gives an energy which smoothly approaches the hydrogen atom eigenvalue of -0.5 a.u. from above.

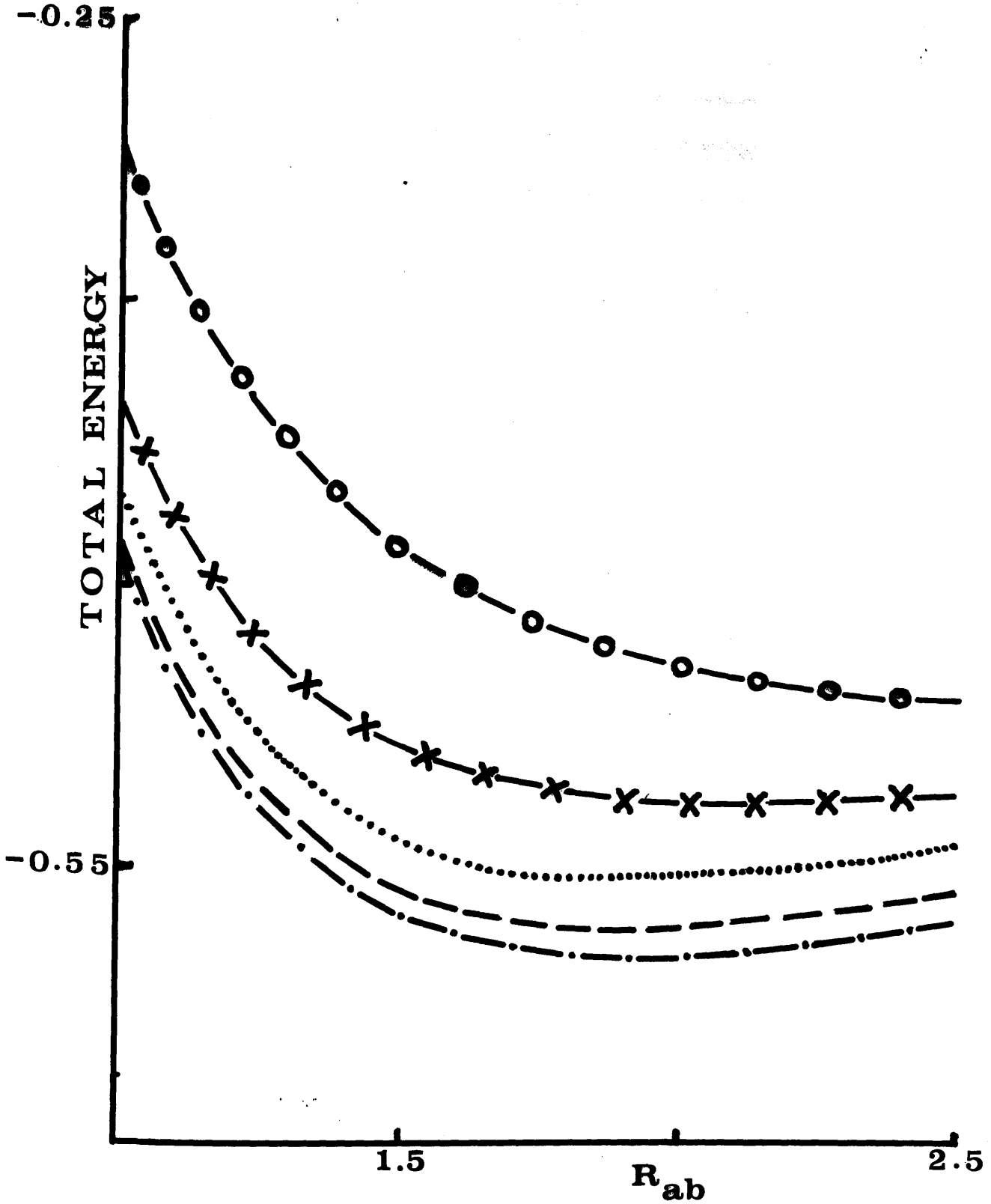
Finally it may be observed that for the longer expansions the convergence with the addition of successive harmonics is exceed--ingly slow for any but the shortest internuclear distances. This is probably a result of greater coupling between the different harmonics than for the united atom method as the earlier terms are steadily modi--fied so that the wavefunction gradually adopts the symmetry of the system. It is thus not surprising that the extrapolation process is not notably reliable as the representation of the cusp at b is probably com--paratively unimportant energetically for the expansion lengths employed.

D Results for HeH^{++}

To conclude this part of the Chapter some single-centre results for HeH^{++} will be related. For this system the choice of an expansion centre on one of the nuclei is physically more appealing than for a homonuclear molecule. In addition if the expansion is made about

Figure 4.5

The total ground state energy for H_2^+ for successive limits employing one of the nuclei as an expansion centre:- S limit —O—O— ; P limit — X — X — ; D limit ..... ; F limit — — — — ; G limit — . — . —;


-0.25
TOTAL ENERGY
-0.55
1.5
2.5
R_{ab}

the He nucleus even for large R_{ab} reliable results might be expected since HeH^{++} gives the products He^{+} and H^{+} on dissociation.

Calculations were performed to attempt to confirm the above point and in Table 4.15 the results for expansion lengths of up to 7 terms are collated with the exact results of Bates and Carson (B4). Although the error at all R_{ab} is not large for either the I limit or the extrapolated energies particular accuracy is found for the extremes of short and long internuclear distances. The reason for this effect is apparent from examination of the detailed analysis of the contribution of each harmonic to the energy in Table 4.16:- For small R_{ab} is almost spherical as the system tends to the united Li^{++} ion while at larger internuclear distances this contribution is again dominant but the system corresponds to that of a He^{+} ion polarised by a proton. With regard to this last remark it may be noted that the increment to the energy for R_{ab} = 5.0 a.u. on the addition of p type polarisation to the spherical wavefunction is -0.00022_6 a.u. which agrees within the expected numerical error with the value of $-2.25/(Z_a R_{ab})^4$ = -0.000225 a.u. evaluated from the expression $B_4 R^{-4}$ for the charge-induced dipole interaction energy for a hydrogenic system and a point charge at long range (similar results are found for other large R_{ab}). At intermediate R_{ab} it may finally be observed that harmonics of high ℓ are again required to build up the charge density about the H nucleus though this is not nearly so marked as for the various calculations on H_2^+.

To conclude the result of the injudicious choice of the H nucleus as the expansion centre is recorded in Table 4.17. For small R_{ab} this does not have too drastic an effect although the angular limits are inferior to those obtained from expanding about the other nucleus. At greater R_{ab} the convergence rate is hopelessly slow for

Table 4.15 The eigenenergies for HeH^{++} at R_{ab} = 0.5, 1.0, 2.0 and 5.0 a.u. using expansion lengths up to 7 terms (expansion centre is on He nucleus).

R_{ab}	0.5	1.0
S limit	-3.537319	-2.951680
P limit	-3.628958	-3.001415
D limit	-3.651846	-3.018199
F limit	-3.659260	-3.025300
G limit	-3.662206	-3.028678
H limit	-3.663576	-3.030438
I limit	-3.664292	-3.031428
Extrapolant	-3.665405	-3.032967
Exact (B4)	-3.66555	-3.03336

R_{ab}	2.0	5.0
S limit	-2.499211	-2.200010
P limit	-2.507516	-2.200236
D limit	-2.509716	-2.200245
F limit	-2.510690	-2.200246
G limit	-2.511217	-2.200246
H limit	-2.511530	-2.200246
I limit	-2.511726	-2.200247
Extrapolant	-2.512028	-2.200247*
Exact (B4)	-2.51220	-2.20024

* Residual error removable by use of greater no. of strips in the calculation.

Table 4.16 An analysis of the energies obtained for HeH^{++} in the one-centre approach using up to 4 terms in the expansion of the wavefunction.

R_{ab}	S Limit	Δ%[a]	P Limit	Δ%	D Limit	Δ%	F Limit	Δ%
0.25	-4.035656	97.6	-4.115558	1.9	-4.128208	0.3	-4.131389	0.1
0.5	-3.537312	96.5	-3.628951	2.5	-3.651839	0.6	-3.659253	0.2
0.75	-3.190653	96.6	-3.262564	2.2	-3.284651	0.7	-3.293051	0.3
1.0	-2.951674	97.3	-3.001409	1.6	-3.018193	0.6	-3.025294	0.2
1.5	-2.660573	98.7	-2.681145	0.8	-2.687920	0.3	-2.691061	0.1
2.0	-2.499206	99.5	-2.507511	0.3	-2.509710	0.1	-2.510685	0.1
2.5	-2.399899	99.8	-2.403528	0.2	-2.404223	0.0	-2.404488	0.0
3.0	-2.333325	99.9	-2.335092	0.1	-2.335329	0.0	-2.335401	0.0

[a] Percentage of the electronic energy (relative to the results of Bates and Carson (B4)) gained with the addition of each harmonic.

Table 4.17 S to I limits for the electronic energy of HeH^{++} using the H nucleus as the expansion centre.

R_{ab}	0.5	1.0	2.0	5.0
S limit	-2.985393	-2.162401	-1.463097	-0.899906
P limit	-3.389110	-2.503326	-1.647279	-0.917124
D limit	-3.542567	-2.706940	-1.816838	-0.942072
F limit	-3.604210	-2.828604	-1.966927	-1.035487
G limit	-3.631481	-2.900878	-2.088522	-1.156818
H limit	-3.644904	-2.944499	-2.182745	-1.269593
I limit	-3.652162	-2.971604	-2.254470	-1.370652
Total energy[a]	0.347838	-0.971604	-1.254470	-1.127781
Exact electronic energy of $1s\sigma$ state[b]	-3.66555	-3.03336	-2.51220	-2.20024
Exact electronic energy of $2p\sigma$ state[b]	-1.19776	-1.33834	-1.34519	-0.92255

[a] Taken from I limit.

[b] Reference (B4).

practical calculation with indeed the appearance of a spurious minimum in the total energy curve.

4.7 Application of the one-centre method in generalised systems

In this final section of Chapter 4 the possibilities of extending the one-centre method to the accurate calculation of electronic energies in more general molecular systems will be briefly considered with of course emphasis on the practicability of employing numerical methods for this task.*

For one-electron molecules from the work presented here it would seem that there are broadly two aspects which give slow convergence of a single-centre expansion of the molecular wavefunction, these being:

1/ The difficulty in reproducing a dissymmetrical charge distribution about the expansion centre e.g. in heteronuclear diatomics as considered in Section 4.6.

2/ The problem of representing a cusp at a nucleus.

In practice, as has been seen, the above cannot be readily separated with the exception of the π states of H_2^+ for which the nuclear singul-arity problem does not occur. Neither can their relative importance be assessed easily for any particular problem. In certain cases it is however possible to see that one of the effects occurs to a minimal

* "Accurate" in this context implies the inclusion of correlation at least to some extent for systems containing two or more electrons.

extent and in general for this type of situation the one-centre approach appears to yield satisfactory results e.g. in one-electron diatomics at short internuclear distances* ; π states of H_2^+. The importance of such factors can be seen in some results for H_3^{++} in the linear symmetrical geometry presented in Table 4.18. It may be observed that the effect of placing an H nucleus at the expansion centre is to entirely change the convergence properties of the expansion, the contribution of the spherical term to the energy actually rising when R_{ab} increases beyond a certain point in marked contrast to the calculations on H_2^+ given in Table 4.1 (cf. results for HeH^{++}). Conversely it is also evident that when both problems occur to a significant extent then it may not be possible to obtain sufficiently converged results with the limited expansions which must be used in practice (the off-centre hydrogen atom problem exemplifies this excellently**). Clearly then before commencing any calculation careful thought must be given to deciding whether the problem is reasonably well-posed or otherwise disappointing results must be anticipated.

For molecules containing more than one electron the comput--ations obviously become much more complicated with the necessity to allow for electron-electron interaction. For highly accurate studies

* Cf. CH_4 for which, as the charge distribution is to an excellent approximation spherical, very good single-centre SCF calculations can be performed (B10).

** At present some calculations on π states of one-electron diatomics employing an expansion centre on one of the nuclei are being instituted in an attempt to further investigate the energetic importance of the nuclear cusps. See Addenda and Corrigenda.

Table 4.18 The S to K limits for the electronic energy for the H_3^{++} system in the linear symmetrical geometrical configuration. The total energy for the K limit is also included.

System length	1.0	2.0	4.0
S limit	-2.985391	-2.162400	-1.463096
	(98.0)[a]	(96.5)	(96.4)
D limit	-3.040275	-2.223384	-1.500200
G limit	-3.047572	-2.236001	-1.513394
I limit	-3.049353	-2.239662	-1.518731
K limit	-3.049976	-2.241040	-1.521125
Total energy[b]	1.950024	0.258960	-0.271125

System length	6.0	8.0
S limit	-1.161617	-0.999298
	(97.4)	(98.8)
D limit	-1.178033	-1.005252
G limit	-1.185993	-1.008309
I limit	-1.190416	-1.010480
K limit	-1.192881	-1.012005
Total energy[b]	-0.359547	-0.387005

[a] Percentage of electronic energy given by S limit.

[b] Taken from K limit.

as well as the two problems discussed in the previous paragraph one also has the need to represent the correlation cusp (see Chapters 2 and 3) and this, combined with the generally increased dimensionality of the calculation, would at first appear to give insurmountable difficulties. Nevertheless even in these unfavourable circumstances it would appear that very precise calculations are possible if the subject is judiciously selected. For example the results of Hoyland (H9) for states of H_2 are encouraging though this author found a very slow term--inal convergence rate.

The above example involving the variational determination of a correlated single-centre wavefunction is though probably except--ional and in general for many-electron molecules one will have to con--template the use of perturbation theory. Double perturbation theory would appear to be especially useful, the perturbations being to correct for correlation between the electrons and to allow for the departure of the molecular wavefunction from the zeroth charge distribution specifically from sphericity. Zeroth wavefunctions containing components which in part accomodate these effects may be considered with however the particular scheme adopted depending on the relative importance of these two perturbations for the system under examination as in for example the treatment of various molecules by Kelly (K9, K10) using many-body perturbation theory.

As an illustration of these points and also to indicate the means by which numerical methods can usefully be utilised in such studies it is instructive to now examine a variation of the double perturbation approach to two-electron diatomics introduced by Chisholm and Lodge (C3):-

For HeH^+ a double perturbation scheme is here developed

employing the Hartree Hamiltonian and wavefunction for He in zeroth order. The zeroth equation can be written as (20) with the perturbations (21) and (22).

$$(H_o^o - E_o^o)\psi_o^o$$

$$= \left(\sum_{i=1}^{2} \left(-\tfrac{1}{2}\nabla_i^2 - Z/r_{iHe} + \int \phi_{1s}^2(3)\, r_{i3}^{-1}\, d\tau_3 - \varepsilon_{1s}^o \right) \psi_o^o \right) = 0 \qquad (20)$$

$$H_o^1 = - \sum_{i=1}^{2} r_{iHe}^{-1} = - \sum_{i} \sum_{\ell} \frac{r_{i<}^{\ell}}{r_{i>}^{\ell+1}} P_\ell(\cos\Theta_i) \qquad (21)$$

$$H_1 = r_{12}^{-1} - \sum_{i=1}^{2} \int \phi_{1s}^2(3)\, r_{i3}^{-1}\, d\tau_3 \qquad (22)$$

Through second order the energy can be summed as in (23).

$$E = E_o^o + E_1^o + E_2^o + E_o^1 + E_o^2 + E_1^1 \qquad (23)$$

The first two terms are obviously the Hartree (or Hartree-Fock) energy of He while the third is the second order correlation energy correction for He evaluated in Chapter 2. E_o^1 can easily be found from (24), this being a correction only for the spherical component of the other nucleus.

$$E_o^1 = \langle \psi_o^o | H_o^1 | \psi_o^o \rangle \qquad (24)$$

To treat the final two terms the perturbed function ψ_o' is taken to be of the form (25), single-particle excitations being induced by the field of the H nucleus.

$$\psi_o' = \chi(1)\ \phi_{1s}(2) + \phi_{1s}(1)\ \chi(2) \qquad (25)$$

Insertion in the perturbation equation (26) yields two identical equations of the type (27) since only one-body terms appear in the perturbation equation.

$$(H_o^o - E_o^o)\,\psi_o' = (E_o^1 - H_o^1)\,\psi_o^o \qquad (26)$$

$$\left(-\tfrac{1}{2}\nabla_1^2 - Z/r_{1He} + \int \phi_{1s}^2(3)\ r_{13}^{-1}\ d\tau_3 - \varepsilon_{1s}^o\right)$$
$$= (\varepsilon_o^1 + r_{1H}^{-1})\ \phi_{1s} \qquad (27)$$

Expansion of the nuclear attraction term in the inhomogeneity as in (21) gives straighforwardly a set of decoupled differential equations for the components of the first order wavefunction:-

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}k(k+1)\,r^{-2} + J_{ls}(r) - Z/r - \varepsilon^{o}_{ls} \right) f_k(r)$$

$$= \left(\varepsilon^{1}_{o}\,\delta_{ko} + \frac{r^{k}_{<}}{r^{k+1}_{>}} \right) R_{ls}(r) \qquad (28)$$

Hence E^2_o can be obtained as a sum of partial wave contributions.*

Finally E^1_1 is in this case zero as can be explicitly shown by substitution of H_1 and Ψ'_o into (29), the disappearance of this contribution being an interesting example of a Brillouin type of theorem (B13).

$$E^1_1 = 2.0 \left\langle \Psi'_o \middle| H_1 \middle| \Psi^o_o \right\rangle \qquad (29)$$

Calculations of the above type were performed for HeH^+ and a number of other systems using the above scheme, one based on a HF rather than a Hartree Hamiltonian and also the original approach of Chisholm and Lodge (C3) which employs a hydrogenic formalism. The numerical procedures used were very simple with a 'square root' grid

* In solving for this term partial waves up to $\ell = 9$ were determined and then energies of partial waves with greater ℓ were found by extrapolation, a terminal convergence rate ℓ^{-4} being apparent from the computed $\varepsilon^{21}(\ell)$.

Table 4.19 A comparison of results for the total energies of HeH^+ using the double perturbation scheme described in the text.

	Perturbation scheme					
R_{ab}	Hydrogenic[a]	Screened[b]	Hartree[c]	Hartree-Fock[c]	CI[d]	HF[e]
0.5	-1.9296	-1.9276	-2.0523	-1.8905	-1.9323	-
0.75	-2.6551	-	-2.7208	-2.6196	-	-
1.0	-2.8632	-2.8747	-2.9065	-2.8382	-2.8955	-2.8610
1.2	-2.9143	-2.9300	-2.9506	-2.8983	-2.9529	-2.9174
1.3	-2.9242	-2.9411	-2.9583	-2.9121	-2.9642	-2.9282
1.4	-2.9289	-2.9462	-2.9611	-2.9198	-2.9691	-2.9326
1.5	-2.9304	-2.9475	-2.9607	-2.9237	-2.9697	-2.9328
1.6	-2.9299	-2.9465	-2.9584	-2.9251	-2.9677	-2.9305
1.7	-2.9285	-2.9442	-2.9552	-2.9249	-	-2.9265
1.8	-2.9267	-2.9413	-2.9514	-2.9238	-	-2.9217
2.0	-2.9227	-2.9348	-2.9437	-2.9203	-2.9495	-2.9112
2.5	-2.9151	-2.9220	-2.9285	-2.9113	-	-2.8888
3.0	-2.9114	-2.9151	-2.9199	-2.9057	-2.9145	-
3.5	-2.9097	-2.9117	-2.9155	-2.9027	-	-2.8686
4.0	-2.9088	-2.9100	-2.9132	-2.9012	-2.9025	-2.8653

[a] This work and reference (C3). Numerical and analytical results are identical.

[b] Reference (C3). [c] This work. [d] Single centre CI calculation of Stuart and Matsen (S27).

[e] Hartree-Fock calculation of Peyerimhoff (P4).

Figure 4.6

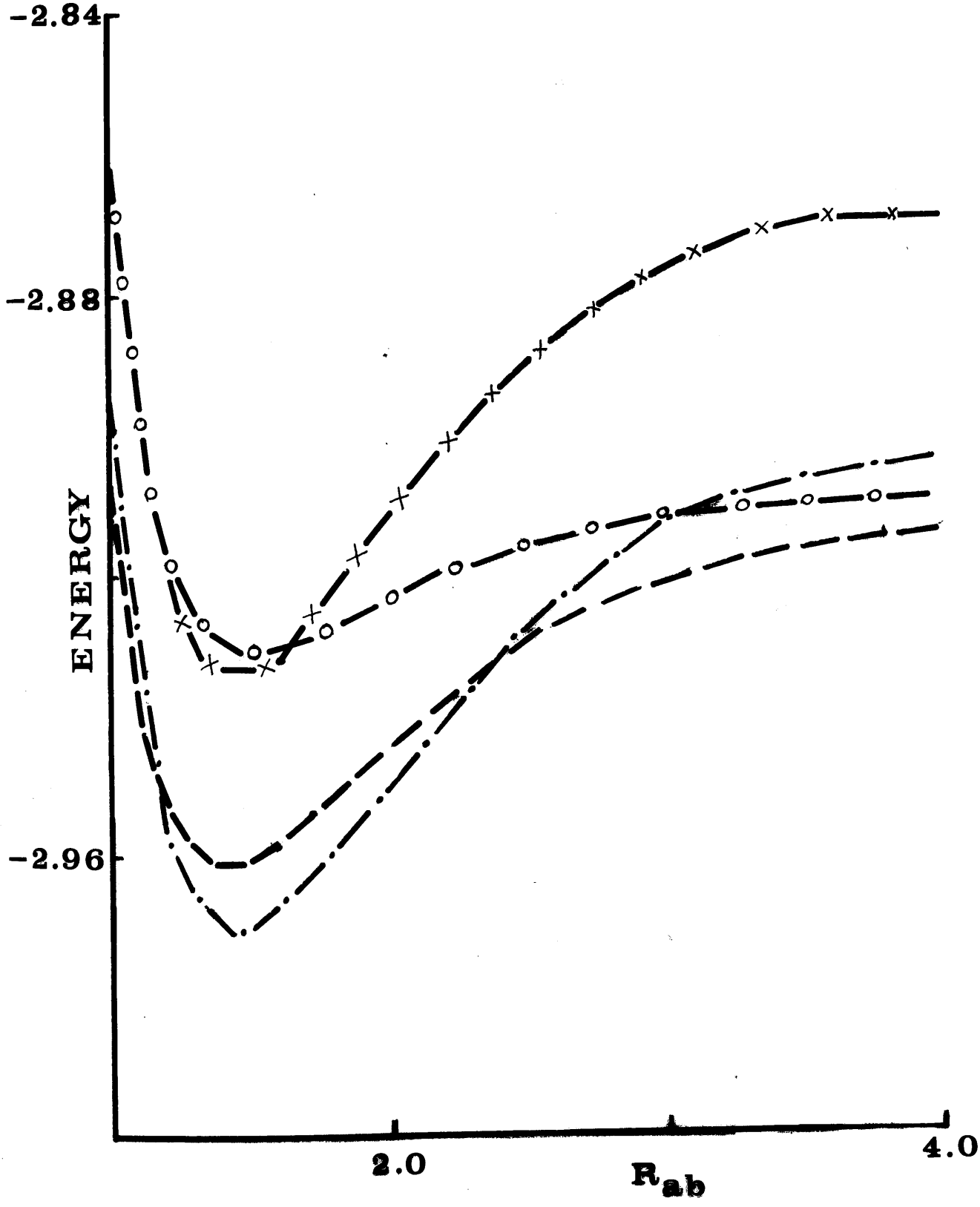
A comparison of results for the total energy of HeH^+:

Double perturbation approach, hydrogenic zeroth Hamiltonian — 0 — 0 — ;

HF SCF results of Peyerimhoff (P4) — X — X — ;

Double perturbation approach, Hartree zeroth Hamiltonian — — — ;

Stuart & Matsen (S27), single-centre CI calculation — . — . — ;


-2.84
-2.88
-2.96
ENERGY
2.0
4.0
R_{ab}

containing 500 strips being utilised for the computation, it not being found necessary to use the Richardson process for the accuracy required.* Results of the work for HeH^+ are given in Table 4.19 together with those from a variety of other methods. It may be observed from that Table and from Figure 4.6 that the Hartree calculations reproduce the potential curve comparatively well except at short internuclear distances as might be expected since HeH^+ corresponds for a wide range of R_{ab} to a good approximation to an He atom polarised by a proton.** It may finally be remarked that there is no guarantee that the computed energy for any of the schemes will not lie below the true energy for any R_{ab} since only contributions through second order have been calculated. The evaluation of third order energies is however apparently hopelessly complicated using analytical methods but may be tractable employing the much simpler finite-difference approach. This problem is at present under investiga--tion.

In conclusion to this section and to this Chapter it may thus be said that it should be possible to extend accurate single-centre cal--culations to a variety of molecular systems in different states. It is difficult though to visualise a unified approach which will generally yield satisfactory results and hence it will probably be necessary to tailor methods, particularly perturbation schemes, to the specific

* Cf. the simplicity of this approach with the analytical method of Chisholm and Lodge which is only practicable for the hydrogenic calculation.

** For large R_{ab} the Hartree scheme corresponds to the uncoupled Hartree method of evaluating static polarisabilities discussed in the next Chapter while the HF scheme is equivalent to the DUHF method.

problem. However it is felt that numerical techniques of the type examined in this Chapter are well suited for this purpose owing to their simplicity and flexibility.

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Chapter 5 A Finite-Difference Approach to the Non-Empirical Calculation of Atomic Polarisabilities.

5.1 Introduction

In previous Chapters first order perturbation theory has been used extensively for the accurate calculation of the correlation energy in various atomic systems. Very many other properties of atoms and molecules can also be computed using low order perturbation theory but unfortunately the perturbation equations frequently cannot be solved satisfactorily employing conventional techniques. For example the very commonly used variational method has several disadvantages such as the difficulty in choosing a suitable set of basis functions to represent the first order perturbed function. Despite the extensive work of Sternheimer* numerical methods have not perhaps been utilised as often as might be expected for this type of problem for which, in the opinion of the author, they are most appropriate. Accordingly in this Chapter it is intended to demonstrate that simple finite-difference techniques can be used to compute accurately the static and dynamic polarisabilities of small atomic systems within diverse approximate, but non-empirical, schemes.

In the first part of this Chapter the static multipole polarisabilities through to $\ell = 5$ are evaluated for two-electron atoms and ions within the CPHF, DUHF and uncoupled Hartree approaches with, in the appropriate cases, first order correlation corrections being

* See for example (S25, S26) and previous references contained therein.

calculated. In particular the latter quantities are investigated caref--ully in an attempt to illuminate the 'geometric approximation' due to Schulman and Musher (S7). In this approximation these authors suggested that the double perturbation series with perturbations of the electric multipole field and of electron correlation can be summed geometrically i.e. $\alpha_{geom} = \alpha_o(1 - \alpha_1/\alpha_o)^{-1}$. Later Tuan (T1) predicted that α_{geom} should be close to the CPHF value but however the limitations on the accuracy of most polarisability calculations make it difficult to give an unequivocal judgement on the range of validity of such an expression. It is intended to remove this uncertainty for two-electron atomic systems.

After further discussion of static polarisabilities for these atoms and ions a direct extension to the frequency-dependent case is given. It is shown that the uncoupled Hartree approximation pervers--ely yields values for the resonances in the anomalous dispersion region of the spectrum for He and Li^+ which are in better agreement with exper--iment than those from the coupled approach.

For systems containing more than two electrons the labour involved in solving the CPHF equations rises extremely rapidly and, even with an efficient computational method, such calculations are only feas--ible at present for small atoms and molecules. There are however a number of possible simplifications of the CPHF approach which result in a considerable reduction of the effort required to determine the 2^l pol--arisabilities of a many-electron atom and hence it becomes possible to consider evaluating this property for quite large systems. To gauge the soundness of such approximations calculations of the dipole and quadru--pole polarisabilities of the members of the beryllium isoelectronic sequence are described within two schemes:-

1/ The DUHF approximation, first order corrected for correlation with/ without application of the geometric approximation.

2/ Method b in the notation of Langhoff, Karplus and Hurst (L4) but which is described here as the Simplified Coupled Perturbed Hartree-Fock (SCPHF) method. In this scheme intrashell coupling is retained but intershell terms are neglected giving a considerable, but physically reasonable, simplification.

Both these methods will be shown to give results which do not differ greatly from the accurate fully coupled results of other workers though the second approximation appears more accurate for the dipole polarisa-bilities. For the latter the negligible effect of intershell self-consistency is also demonstrated in the calculation of dynamic polarisabilities in the four-electron series, the dipole spectrum of the beryllium atom being chosen as an apposite example.

A summarising discussion, with projections of future possible research, will conclude this Chapter.

5.2 Theory and numerical methods for two-electron systems: SCF approaches.

A Derivation of the perturbation equations

Consider the perturbation (1) which is a sum of one-electron operators and the perturbed system which is approximated in zeroth order by a single determinant wavefunction (2) which is an eigen-function of the Hartree-Fock Hamiltonian (3).

$$H' = \sum_{j=1}^{N} h'(j) \tag{1}$$

$$\Psi^{o} = A\left(\prod_{j=1}^{N} \chi_j^{o}\right) \tag{2}$$

$$H^{o} = \sum_{j=1}^{N} h^{o}(j) \tag{3}$$

where the spin orbital χ_j^{o} is an eigenfunction of the single-particle operator (4).

$$h^{o}(1) = -\tfrac{1}{2}\nabla_1^2 - Z/r_1 + \sum_{i=1}^{N} \left\langle \chi_i^{o} \left| r_{12}^{-1}(1 - P_{12}) \right| \chi_i^{o} \right\rangle \tag{4}$$

Now writing the first order perturbed wavefunction as in (5) and inserting it in the perturbation equation (6) furnishes the Coupled Perturbed Hartree-Fock (CPHF) equations for the perturbed orbitals (L4, T2).

$$\Psi' = \sum_{j=1}^{N} A\left(\prod_{i\neq j}^{N} \chi_i^{o}\, \chi_j^{1}\right) \tag{5}$$

$$(H^{o} - EO)\,\Psi' = (E1 - H')\,\Psi^{o} \tag{6}$$

$$\begin{aligned}&(h^{o}(1) - \varepsilon_j^{o})\,\chi_j^{1}(1)\\ &+ \sum_{i=1}^{N} \left(\left\langle \chi_i^{1} \left| r_{12}^{-1}(1 - P_{12}) \right| \chi_i^{o} \right\rangle + \left\langle \chi_i^{o} \left| r_{12}^{-1}(1 - P_{12}) \right| \chi_i^{1} \right\rangle \right) \chi_j^{o}(1)\\ &= (\varepsilon_j^{1} - h'(1))\,\chi_j^{o}(1)\end{aligned} \tag{7}$$

The perturbing operator for the 2^{ℓ} polarisability is taken as (8) and with the employment of (9) for the space part of the perturbed orbital the equation (10) is easily obtained for the radial function $f_\ell(r)$ for the particular case of the two-electron sequence.

$$h'(1) = r_1^{\ell} P_\ell(\cos\Theta_1) \tag{8}$$

$$\underline{\Phi}' = r^{-1} f_\ell(r) (4\pi)^{\frac{1}{2}} P_\ell(\cos\Theta) \tag{9}$$

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1) r^{-2} - Z/r + \int P_{1s}^2(r') r^{-1} dr' - \varepsilon_{1s}^{o} \right) f_\ell(r)$$
$$= -\left(r^{\ell} + 2(2\ell+1)^{-1} \int P_{1s}(r') f_\ell(r') \frac{r_<^{\ell}}{r_>^{\ell+1}} dr'\right) P_{1s}(r) \tag{10}$$

The polarisability is given as a sum of one-electron operators (11), E1 being zero for this perturbation. The reduction of this expression to one involving the radial functions P_{1s} and f_ℓ is obvious.

$$= -2.0 \sum \left\langle \chi_j^{o} \middle| h' \middle| \chi_j^{1} \right\rangle \tag{11}$$

Omission of the second term on the L.H.S. of (7) yields the Dalgarno Uncoupled Hartree-Fock (DUHF) approximation which in alternative notation gives a radial equation (12), J(r) and K(r) being Coulomb and exchange operators respectively.

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} - Z/r + 2\,J(r) - K(r) - \varepsilon^{o}_{ls} \right) f_{\ell}(r) \quad (12)$$

$$= -r^{\ell} P_{ls}(r)$$

Finally development of the theory based on a Hartree rather than a Hartree–Fock formalism gives the uncoupled Hartree scheme for which, for two-electron systems, the radial equation for the perturbed orbital is (13):-

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} - Z/r + J(r) - \varepsilon^{o}_{ls} \right) f_{\ell}(r)$$

$$= -r^{\ell} P_{ls}(r) \quad (13)$$

B First order correlation corrections and the geometric approximation

As has been discussed by Jamieson (J1) the CPHF approach contains some allowance for electron correlation. The uncoupled methods are deficient in this respect but however they can be considerably improved by the use of double perturbation theory. For example for the uncoupled Hartree method if the two perturbations (14) and (15) are considered then the polarisability to first order in electron correlation is $\alpha = \alpha_o + \alpha_1$.

$$H^{01} = \sum_{j=1}^{N} h'(j) \quad (14)$$

$$H^{10} = r_{12}^{-1} - J(r_1) - J(r_2) \quad (15)$$

a_o is the polarisability calculated as described in the previous section while a_1, as shown by Schulman and Tobin (S8), is evaluated as:

$$a_1 = -2\, E_{12} = -2 \left\langle \Psi^{01} \mid H^{10} - E^{10} \mid \Psi^{01} \right\rangle \qquad (16)$$

$$= -8 \left\langle \phi^1(1)\ \phi^1(2) \mid r_{12}^{-1} \mid \phi^o_{1s}(1)\ \phi^o_{1s}(2) \right\rangle \qquad (17)$$

For the DUHF approximation the theory is entirely analogous and a_1 is given by (18).

$$a_1 = 4 \left\langle \phi^1(1)\ \phi^o_{1s}(2) \mid r_{12}^{-1} \mid \phi^1(1)\ \phi^o_{1s}(2) \right\rangle$$
$$-12 \left\langle \phi^1(1)\ \phi^1(2) \mid r_{12}^{-1} \mid \phi^o_{1s}(1)\ \phi^o_{1s}(2) \right\rangle \qquad (18)$$

Now it is known that the uncoupled approaches, even when corrected as above, are generally less accurate than the fully coupled method (E1, S8). However Schulman and Musher (S7) have noted that the uncoupled values can be improved by the 'geometric approximation' i.e. the higher terms in the double perturbation series are approximately accounted for by assuming that the series is geometric and can be summed thus as in (19).

$$a_{geom} = a_o\,(1 - a_1/a_o)^{-1} \qquad (19)$$

Tuan (T1) has predicted that a_{geom} should be close to a_{CPHF} in many

cases. As noted by this author variational methods have been generally used in the evaluation of polarisabilities with a consequent uncertainty in the values of α_{geom} and α_{CPHF} due to the necessary truncation of the basis set for the perturbed orbitals. In this study this deficiency is removed by calculating α_0 and α_1 numerically to a high degree of accuracy.

C Numerical methods

To solve the inhomogeneous differential equations (10), (12) and (13) a computational scheme of modest complexity of a type previously described was employed. Using a three point finite-difference formula for the second derivative the differential equations could be reduced to tridiagonal linear form and solved in the customary manner, the polarisability being found from (11). Such an approach has been used by Schulman and Tobin (S7) in their study of dipole polarisabilities and shielding factors within the uncoupled Hartree method. Although the values of the polarisabilities α_0 derived as described above are of adequate accuracy for many purposes they can be greatly improved by the Richardson extrapolation process, the first order correlation corrections being similarly refined. For the calculations described in this section it was found that with a 'square root' distribution of points a range of grids containing between 60 and 100 strips was more than sufficient and all figures presented here are believed to be accurate within the constraint imposed by the quality of the zeroth functions. It may finally be remarked that for the CPHF and DUHF methods the requisite equations had to be solved iteratively owing to the presence of the exchange terms. As before this did not present any difficulties although the computational effort was necessarily severalfold greater than for the

Hartree equation which involves only local operators.

5.3 Discussion of results for the SCF approaches for the He isoelectronic sequence.

In Table 5.1 the CPHF polarisabilities from $\ell = 1$ through to $\ell = 5$ for the He isoelectronic sequence are listed for Z = 1 to Z = 10 in atomic units. As stated in the preceding section all figures are believed to be accurate with the proviso that the quality of the available zeroth functions may reduce this accuracy somewhat. For this purpose, as for the correlation energy calculations, the analytic orbitals of Clementi (C7) were used with the exception of H^- where that of Curl and Coulson (C11) was employed. In Table 5.2 some of the results of this work are compared with a brief selection of previous computa--tions and it can be seen that the present studies appear to be in har--mony with other accurate CPHF calculations. Also included in the Table are the values of Davison (D10) based on a correlated wavefunction confirming that in general the polarisabilities evaluated using the CPHF method are close to the exact polarisabilities. The sole exception to this is the hydride ion for which, as discussed by Adelman (A3), all of the approximations used here are inadequate.

For He and C^{4+} α_o, α_1 and α_{geom} are given for the 2^ℓ pol--arisabilities in the third and fourth Tables for the uncoupled Hartree and DUHF approximations. It may be observed that whereas α_o and $\alpha_o + \alpha_1$ are superior for the Hartree method the values of α_{geom} differ negligibly. In addition, in accord with the predictions of Tuan (T1), the α_{geom} are identical or almost so with the CPHF results. This is especially noticeable for ℓ greater than one and it is perhaps not

Table 5.1 Multipole polarisabilities calculated within the CPHF approximation for the two-electron sequence ground state. The exponent is given in brackets after the mantissa for each value.

Z	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$
1.0	0.99456(02)	0.30938(04)	0.26269(06)	0.45362(08)	0.12920(11)
2.0	0.13222(01)	0.23260(01)	0.10014(P2)	0.80793(02)	0.10576(04)
3.0	0.18948(00)	0.11212(00)	0.16622(00)	0.46199(00)	0.20932(01)
4.0	0.51872(-1)	0.15296(-1)	0.11568(-1)	0.16674(-1)	0.40173(-1)
5.0	0.19555(-1)	0.34265(-2)	0.15446(-2)	0.13144(-2)	0.18328(-2)
6.0	0.89367(-2)	0.10360(-2)	0.30950(-3)	0.17336(-3)	0.15709(-3)
7.0	0.46455(-2)	0.38244(-3)	0.81221(-4)	0.32187(-4)	0.20463(-4)
8.0	0.26483(-2)	0.16277(-3)	0.25828(-4)	0.76219(-5)	0.25876(-5)
9.0	0.16182(-2)	0.77071(-4)	0.94848(-5)	0.21654(-5)	0.78546(-6)
10.0	0.10437(-2)	0.39650(-4)	0.38948(-5)	0.70853(-6)	0.20423(-6)

Table 5.2 A comparison of CPHF values for the dipole and quadrupole polarisabilities of He and Li^+ with the accurate calculations of Davison (D10) using a correlated wavefunction.

	Dipole polarisability	Quadrupole polarisability
He		
This work	1.3222	2.3260
Other CPHF	1.322_3[a], 1.323[b]	2.326[b]
Davison	1.3796	2.4403
Li^+		
This work	0.18948	0.11212
Other CPHF	0.1894_8[a], 0.1895[b]	0.1120[b]
Davison	0.19223	0.11362

[a] Tuan and Davidz (T2).

[b] Lahiri and Mukherji (L1, L2).

Table 5.3 A comparison of the multipole polarisabilities for He derived from the CPHF, DUHF and uncoupled Hartree approximations.

	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$
Uncoupled Hartree					
α_o	0.14870(1)	0.23591(1)	0.10037(2)	0.80826(2)	0.10577(4)
α_1	-0.19281(0)	-0.34100(-1)	-0.22898(-1)	-0.33560(-1)	-0.85592(-1)
$\alpha_o + \alpha_1$	0.12942(1)	0.23250(1)	0.10014(2)	0.80793(2)	0.10576(4)
α_{geom}	0.13164(1)	0.23255(1)	0.10014(2)	0.80793(2)	0.10576(4)
DUHF					
α_o	0.99722(0)	0.18002(1)	0.83136(1)	0.69000(2)	0.92848(3)
α_1	0.24195(0)	0.40685(0)	0.14764(1)	0.10070(2)	0.11335(3)
$\alpha_o + \alpha_1$	0.12392(1)	0.22070(1)	0.96900(1)	0.79070(2)	0.10418(4)
α_{geom}	0.13167(1)	0.23258(1)	0.10014(2)	0.80791(2)	0.10576(4)
CPHF					
α	0.13222(1)	0.23260(1)	0.10014(2)	0.80793(2)	0.10576(4)

Table 5.4 A comparison of the multipole polarisabilities for C^{4+} derived from the CPHF, DUHF and uncoupled Hartree approximations.

	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$
Uncoupled Hartree					
α_o	0.92913(-2)	0.10408(-2)	0.30973(-3)	0.17338(-3)	0.15709(-3)
α_1	-0.37282(-3)	-0.48051(-5)	-0.23319(-6)	-0.24404(-7)	-0.44018(-8)
$\alpha_o + \alpha_1$	0.89185(-2)	0.10360(-2)	0.30950(-3)	0.17336(-3)	0.15709(-3)
α_{geom}	0.89329(-2)	0.10360(-2)	0.30950(-3)	0.17336(-3)	0.15709(-3)
DUHF					
α_o	0.81758(-2)	0.96038(-3)	0.29251(-3)	0.16592(-3)	0.15160(-3)
α_1	0.69367(-3)	0.70123(-4)	0.16054(-4)	0.71177(-5)	0.52977(-5)
$\alpha_o + \alpha_1$	0.88695(-2)	0.10305(-2)	0.30856(-3)	0.17304(-3)	0.15689(-3)
α_{geom}	0.89338(-2)	0.10360(-2)	0.30950(-3)	0.17336(-3)	0.15709(-3)
CPHF					
α	0.89367(-2)	0.10360(-2)	0.30950(-3)	0.17336(-3)	0.15709(-3)

surprising for the uncoupled Hartree approach as the first order corr-ection is generally small in comparison with a_o. However, for example for the octupole polarisability of He the DUHF a_1 is 18% of a_o and $a_o + a_1$ is still more than 3% different from a_{CPHF}. Yet, remarkably, a_{geom} agrees with the coupled value to five figure accuracy implying that the geometric approximation is a very reliable relationship at least for these simple systems.

It is informative to examine the effect of inaccuracy in the zeroth function on all of the calculated quantities. In Table 5.5 for He are listed the $\ell = 1$ and $\ell = 5$ polarisabilities which have been computed using Clementi's 4 term representation of the 1s orbital rather than the more accurate 5 term basis set. The dipole values differ very little between the two groups of calculations but however the $\ell = 5$ polarisabilities reflect strongly the sensitivity of this property to the "goodness" of the unperturbed functions, the discrepancy being about 30%. Despite this excellent agreement is again found between a_{CPHF} and the geometrically approximated values and it thus may be speculated that in general these quantities will correspond closely provided the same zeroth function is utilised for all calculations.

In some very early work Pauling (P2) suggested, on the basis of a hydrogenic model, that dipole polarisabilities in atomic systems should be inversely proportional to the fourth power of the screened nuclear charge, this having been confirmed by several authors, for example Cohen (C8), for two-electron atoms. It is interesting to extend this discussion a little to other multipoles. For a screened hydrogenic system the static multipole polarisability can be shown, by an elemen-tary calculation, to be given by (20):-

Table 5.5 The $\ell = 1$ and $\ell = 5$ polarisabilities for He using the Clementi 4 term representation of the 1s orbital.

	$\ell = 1$	$\ell = 5$
Uncoupled Hartree		
a_o	0.14967(1)	0.13702(4)
a_1	-0.19280(0)	-0.85445(-1)
$a_o + a_1$	0.12939(1)	0.13701(4)
a_{geom}	0.13160(1)	0.13701(4)
DUHF		
a_o	0.99698(0)	0.12102(4)
a_1	0.24187(0)	0.14095(3)
$a_o + a_1$	0.12389(1)	0.13511(4)
a_{geom}	0.13163(1)	0.13697(4)
CPHF		
a	0.13219(1)	0.13701(4)

$$a_\ell = \ell^{-1}\, 2^{-2\ell}\, (\ell+2)\, (2\ell+1)!\, (Z-\sigma)^{-(2\ell+2)}$$

$$= \tfrac{1}{2} A\, (Z-\sigma)^{-(2\ell+2)} \qquad (20)$$

Now for a two-electron atom a naive hydrogenlike model would yield a value of twice that given by (20) for the 2^ℓ polarisability and hence the latter should be proportional to $(Z-\sigma)^{-2}$ $^{-2}$. Indeed, as can be seen in Figure 5.1, a plot of the appropriate $a^{-1/n}$ versus atomic number is linear. Further in Table 5.6, from a least-square fit of the CPHF data from He to Ne^{8+}, the screening constants σ and the factors A are listed for each ℓ and it may be observed that the A values are surprisingly close to those obtained assuming hydrogenic behaviour. The screening constants are also physically reasonable, increasing with ℓ as the outer parts of the unperturbed wavefunction become more important in the calculation, though unfortunately there does not appear to be any a priori method of estimating the requisite value of σ. It may lastly be noted that the encouraging results recorded by Adelman and Szabo (A5) for the two-electron series using the Coulomb approximation are perhaps not so surprising as at first sight in view of this hydrogenlike behaviour of the polarisabilities for this isoelectronic sequence.

5.4 A digression on the polarisability of a radially correlated two-electron atom.

In Chapter 2 the calculation of correlation energies in two-electron atoms employing perturbation theory based on a radially correlated wavefunction was outlined, the results of such calculations

Figure 5.1

Graphs of the $(2\ell+2)$th root of a_{CPHF} versus atomic number for the He isoelectronic series. Plots for $\ell = 1$, 2 and 3 only are included to avoid unnecessary obfuscation.

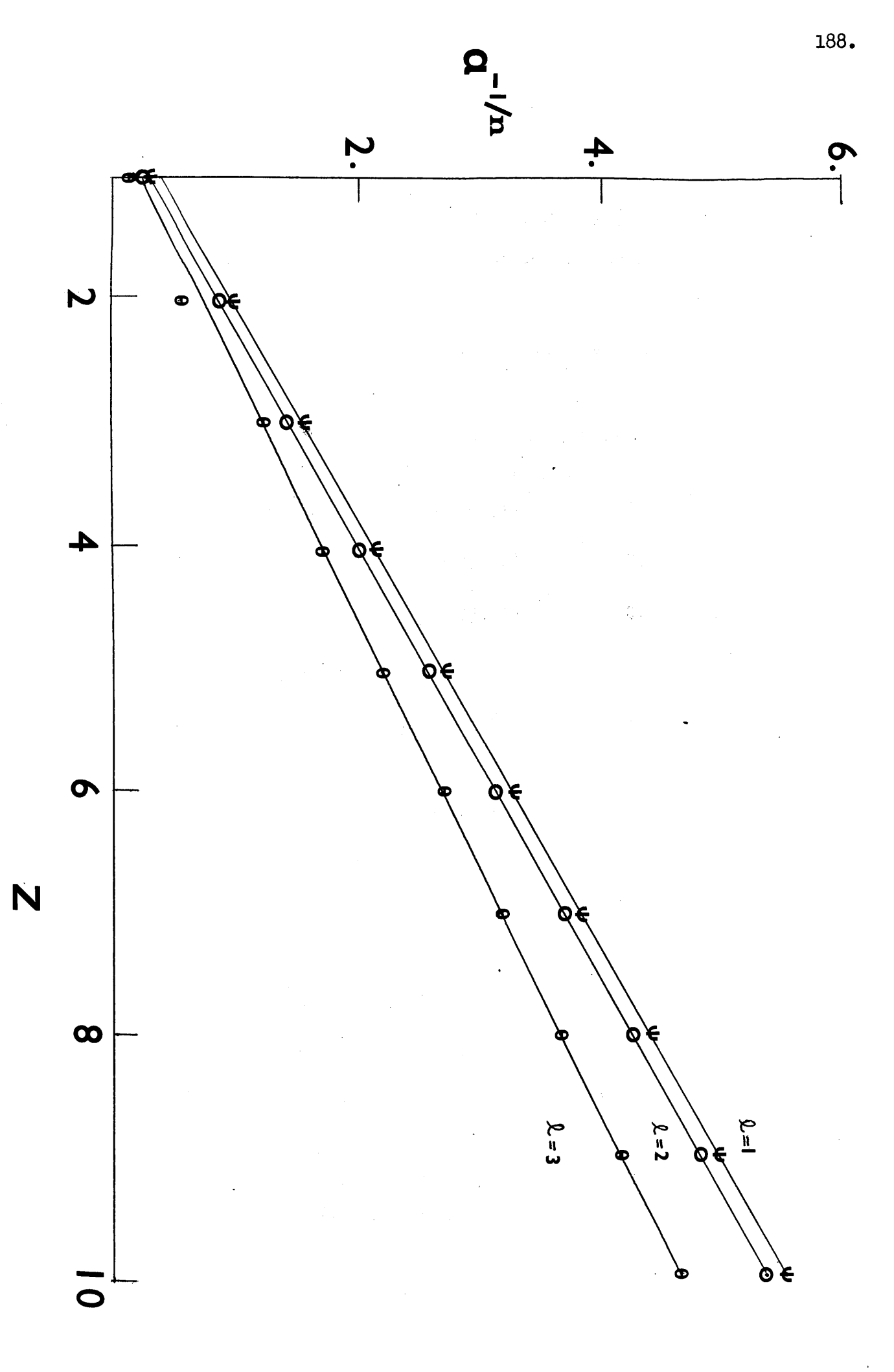

$a^{-1/n}$
2.
4.
6.
Z
2
4
6
8
10
$\ell=1$
$\ell=2$
$\ell=3$

Table 5.6 The values of the factor A and the screening constant derived from the least-square fit of the CPHF polarisa-bilities to the formula $\alpha_\ell = A\,(Z-\sigma)^{-2\ell-2}$. Also included are the A factors appropriate to a hydrogenic system.

ℓ	σ	A	A^H
1	0.382	0.892(1)	0.9(1)*
2	0.468	0.297(2)	0.30(2)
3	0.499	0.259(3)	0.2625(3)
4	0.525	0.416(4)	0.42525(4)
5	0.553	0.105(6)	0.1091475(6)

* A^H are the A factors for a hydrogenic system.

being most encouraging with a very high percentage of E_{corr} being recovered through third order even for H^-. At this point in this Chap-ter on the non-empirical calculation of atomic polarisabilities it is informative to digress briefly from the examination of various SCF approaches and consider a similar scheme, here the perturbation being an electric field rather than the angular terms in the expansion of r_{12}^{-1}.

The S limit wavefunction is an eigenfunction of the Hamiltonian (21).

$$H^o = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + r_>^{-1} \qquad (21)$$

For the perturbation (22) a first order wavefunction can be constructed in the form (23) in which, for consistency, only ℓ type single-particle excitations are allowed.

$$H' = -r_1^{\ell} P_{\ell}(\cos\Theta_1) - r_2^{\ell} P_{\ell}(\cos\Theta_2) \qquad (22)$$

$$\Psi' = (4\pi)^{-1} \left(\psi_{\ell}(r_1,r_2) P_{\ell}(\cos\Theta_2) + \psi_{\ell}^{T}(r_1,r_2) P_{\ell}(\cos\Theta_1) \right) \qquad (23)$$

where

$$\psi_{\ell}(r_1,r_2) = \psi_{\ell}^{T}(r_2,r_1) \qquad (24)$$

Insertion of (23) in the perturbation equation (6) gives a radial equation for $U_{\ell}(r_1,r_2) = r_1 r_2 \psi_{\ell}(r_1,r_2)$ as below on manipulation.

$$\left(-\tfrac{1}{2}\frac{\partial^2}{\partial r_1^2} - \tfrac{1}{2}\frac{\partial^2}{\partial r_2^2} + \tfrac{1}{2}\ell(\ell+1)\, r_2^{-2} - Z/r_1 - Z/r_2 \right.$$

$$\left. + r_>^{-1} - E0 \right) U_\ell(r_1,r_2) = r_1 r_2^{\ell+1}\, \Psi^o(r_1,r_2) \qquad (25)$$

On determination of the solution of this equation the polarisability can be found from the elementary integral (26).

$$a_\ell = +2(2\ell+1)^{-1} \int U_\ell(r_1,r_2)\, r_1 r_2^{\ell+1}\, \Psi^o(r_1,r_2)\, dr_1\, dr_2 \qquad (26)$$

The equation (25) is just a simple elliptic partial diff--erential equation the numerical solution of which has been described several times in this work. For this particular case solutions were found on a linear grid containing 35(5)65 strips using SOR, the S limit functions of Davies (D9) being again employed for Ψ^o.

In Table 5.7 results are given for the dipole and quadru--pole polarisabilities of H^-, He and Li^+ together with some values for these quantities calculated by other approaches. From this comparison it is evident that the S limit polarisabilities must substantially exceed the true values of the a_ℓ, there being poor agreement with either CPHF computations or, for the hydride ion, with the refined calculations of Adelman (A3). Thus the use of a zeroth wavefunction which gives a lower energy than the HF function does <u>not</u> give a better value of a. The present work however gratifyingly gives polarisabilities which do not differ greatly from those of Kolker and Michels (K13) who use an open-shell Ψ^o which contains a considerable measure of radial correl--ation.

Table 5.7 The values of the dipole and quadrupole polarisabilities of H^-, He and Li^+ obtained using the S limit zeroth wavefunction and Hamiltonian. For comparison values of these properties computed using other approaches are included in the Table.

	S limit	Other values		
H^-				
Dipole polarisability	640.6	507.6[a],	99.46[b],	215.5[c]
Quadrupole polarisability	3.960×10^4		3094. ,	7765.
He				
Dipole polarisability	1.584	1.576[a],	1.322[b]	
Quadrupole polarisability	2.636		2.326	
Li^+				
Dipole polarisability	0.2094	0.2067[a],	0.1895[b]	
Quadrupole polarisability	0.1173		0.1121	

[a] Open-shell (partial radial correlation) results of Kolker and Michels (K13).

[b] CPHF values from section 5.3.

[c] Essentially exact refined calculations of Adelman (A3).

The principal fact to emerge from these calculations is the importance of using an initially good charge distribution in the evaluation of polarisabilities using perturbation theory. From the work of Banyard (B1) it is evident that the S limit wavefunction for the hydride ion is much too diffuse in comparison with the exact wave--function and thus the excessive values of the a_ℓ are not unreasonable. similarly the HF function for H^- is too compact and, as indicated by Deal and Kestner (D12), this results in low values for the polarisabil--ities calculated from the various SCF methods. For the other systems the effect becomes less marked as the overall charge distributions for the exact, S limit and HF wavefunctions come more into accord.

Although the above results are perhaps a little disappoint--ing the method used in the calculation may be viewed as a first attempt at the accurate numerical calculation of atomic polarisabilities beyond SCF methods. Obviously both the zeroth and first order functions are expressible in more general CI form. Hence it may be possible to deter--mine the polarisability from a set of coupled partial differential equations analogous to the exact pair equations solved by Winter (W12) although the development will undoubtedly be complicated, perhaps hopelessly so. Finally it may be remarked that even the simple function (22) may perhaps yield good results for systems in which angular corre--lation is unimportant e.g. the He atom in the $1S2S\ ^3S$ state where it comprises less than 1 part in 2000 of the total energy.

5.5 Extension to the frequency-dependent case for two-electron atoms

In this particular section of the thesis the work on static polarisabilities in two-electron systems will be extended to the more

general case in which the perturbation is time-dependent. The resulting dynamic polarisability is of considerable importance since properties such as the refractive index and Verdet constant depend directly on this quantity and can be determined from the latter once its value(s) is known. Unfortunately although the CPHF method and other SCF approaches can be applied to the determination of $\alpha(\omega)$ the resulting equations for the first order wavefunction are somewhat more elaborate than those for the static case and their solution has presented many problems especially in the region of anomalous dispersion. It is thus intended to show here that simple finite-difference techniques can be successfully applied to this problem with little more difficulty than for the less complex calculations studied earlier in this Chapter.

A Theory and numerical methods

Here an atomic system is considered to be perturbed by a time-dependent perturbation (27), the h'(j) still be defined as in (8).

$$H' = (\exp(-i\omega t) + \exp(i\omega t)) \sum_{j=1}^{N} h'(j) \qquad (27)$$

It is now desired to determine the effect of (27) within a framework of HF perturbation theory:- As before, in the absence of the perturbation the system is described by the wavefunction (2) which is an eigen--function of the HF Hamiltonian (3). Following Dalgarno and Victor (D5) the perturbed wavefunction through first order is written as (28).

$$\Psi = \exp(-iE^0 t)\, \underline{A}\, (\prod_{j=1}^{N} (\chi_j^0 + \chi_{j+}^1 \exp(i\omega t) + \underline{\chi}_{j-}^1 \exp(-i\omega t)) \qquad (28)$$

Insertion in the time-dependent equation (29) followed by considerable manipulation yields the CPHF equations (30) for this problem.

$$(H^{o} + H' - i\frac{\partial}{\partial t})\,\Psi = 0 \qquad (29)$$

$$(h^{o}(j) - \varepsilon_{j}^{o} \pm \omega)\,\chi_{j\pm}^{1}(j) + V_{j\pm}^{1}(j)\,\chi_{j}^{o}(j)$$

$$= (\langle \chi_{j}^{o} | V_{j\pm}^{1} | \chi_{j}^{o} \rangle \pm \omega \langle \chi_{j}^{o} | \chi_{j\pm}^{1} \rangle - h'(j))\,\chi_{j}^{o}(j) \qquad (30)$$

where

$$V_{j\pm}^{1}(j) = \sum_{k=1}^{N} (a_{jk\pm}^{1} - \beta_{jk\pm}^{1}) \qquad (31)$$

with

$$a_{jk\pm}^{1} = \int \chi_{k}^{o}(k)\,\chi_{k\pm}^{1}(k) + \chi_{k\mp}^{1}(k)\,\chi_{k}^{o}(k)\,r_{jk}^{-1}\,d\tau_{k} \qquad (32)$$

and

$$\beta_{jk\pm}^{1}\,\chi_{t}(j) = \int (\chi_{k\mp}^{1}(k)\,\chi_{t}(k)\,\chi_{k}^{o}(j) + \chi_{k}^{o}(k)\,\chi_{t}(k)\,\chi_{k\pm}^{1}(j))\,r_{jk}^{-1}\,d\tau_{k} \qquad (33)$$

Broadly it may be observed that the appropriate equation (30) for each perturbed function does not differ greatly from its counterpart (10) for the simpler static problem with however the notable extra complexity that additional terms occur coupling together the χ_{j+}^{1} and χ_{j-}^{1}. This, as will be seen, causes most of the computational problems in the solution of (30). It is perhaps more transparent from the explicit

equations for the two-electron atom resulting from the expression of the first order function in the same angular form as the multipolar operator. On integration over the angular variables the requisite radial equations are as in (34), the frequency-dependent polarisability being a simple generalisation of (11).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\,r^{-2} - Z/r + J_{ls}(r) - \varepsilon^{o}_{ls} \pm \omega \right) f^{\pm}_{\ell}(r)$$

$$= -(r^{\ell}P_{ls}(r) + K_{ls}f^{+}(r) + K_{ls}f^{-}(r)) \qquad (34)$$

where

$$K_{ns}f^{\pm}(r) = (2\ell+1)^{-1}\,P_{ns}(r)\int P_{ns}(r')\,f^{\pm}(r')\,\frac{r_{<}^{\ell}}{r_{>}^{\ell+1}}\,dr' \qquad (35)$$

As before it is possible to develop various uncoupled approaches which are approximations to (35) which are substantially simpler to handle than the coupled scheme. For example for the uncoupled Hartree method it is only necessary to determine solutions to (36).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\,r^{-2} - Z/r + J_{ls}(r) - \varepsilon^{o}_{ls} \pm \omega \right) f^{\pm}_{\ell}(r)$$

$$= -\,r^{\ell}\,P_{ls}(r) \qquad (36)$$

The numerical solution of the equations for the uncoupled methods presents no difficulties though the computational labour is double that required to compute $\alpha(0)$ as it is necessary to solve for $f^{+}(r)$ and $f^{-}(r)$. The scheme used for the calculations was exactly as

described in 5.2 for static polarisabilities, comparable precision being believed to be maintained. A useful check on this last point is afforded by the calculation of the dynamic polarisability of the hydrogen atom for which an exact solution is known. For this problem it is required to solve the equations (37) which are clearly analogous to (36).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} - r^{-1} + 0.5 \pm \omega \right) f_\ell^{\pm}(r)$$

$$= -2.0\, r^{\ell} \exp(-r) \qquad (37)$$

Calculations were executed for this system for a wide range of frequencies using a series of grids containing up to 500 strips, suitable radial cutoffs being chosen. In Table 5.8 extrapolants from the primitive values of the dynamic dipole polarisabilities are given together with exact values of this quantity, the variational results of Karplus and Kolker (K3) and the most refined $\alpha(\omega)$ of Alexander and Gordon (A6) derived by a numerical process which is entirely different from that employed in this work. With regard to the present work it is sufficient to note that seven to eight figure accuracy is obtained even in the proximity of the resonances, no other computational method giving an improvement on this.

For the coupled equations it is necessary to follow an iterative scheme which is rather similar to that utilised in the DUHF calculations but which involves the simultaneous determination of $f^{+}(r)$ and $f^{-}(r)$ due to the coupling between the radial equations. However, as has been found by other workers (J1, A7), close to the poles the simple iterative method does not converge with a strongly oscillating divergence being generally observed. Two approaches have been proposed to

Table 5.8 A comparison of values of the frequency-dependent polarisability of the hydrogen atom calculated within various computation schemes. A conversion factor of 1 a.u. = 455.6345 Angstroms has been used for these computations.

ω(Å)	Present work	Exact (K3)	Variational[a] (K3)	Alexander & Gordon (A6)
∞	4.5000000	4.5	4.500(2)	4.5000000
6000.0	4.6592576	4.6592576	4.659(4)	4.6592576
3000.0	5.2217822	5.2217822	5.222(4)	5.2217822
1250.0	56.915235	56.915233	56.915(9)	56.915228
1220.0	367.16785	367.16784	367.17(13)	367.16715
1210.0	-351.96273	-351.96274	-351.96(12)	-351.96295
1180.0	-45.174976	-45.174976	-45.175(11)	-45.174986
1100.0	-7.5233269	-7.5233269	-7.523(19)	-7.5233280
1060.0	0.19555431	0.1955543	0.195(20)	0.1955537
1040.0	9.9156120	9.9156118	9.913(20)	9.9156104
1030.0	39.494174	39.494172	-	39.494141
1020.0	-41.815141	-41.815141	-	-41.815146
1010.0	-14.680592	-14.680592	-	-14.680591
990.0	-3.7036796	-3.7036796	-	-3.7036788
980.0	2.9146505	2.9146505	-	2.9146471
974.0	28.440270	28.440272	-	28.440264
970.0	-34.878007	-34.877999	-	-34.878001
965.0	-11.108817	-11.108812	-	-11.108814

[a] Number of terms in the expansion of the perturbed function are included in brackets.

eliminate this problem:-

1/ The first of these is to recast the radial equations so that a non-iterative scheme can be used. In this manner the CPHF equations have been solved for two-electron atomic systems by Jamieson (J1), this author employing the Numerov stepwise integration process. The great disadvantage of this approach though is that additional coupled equa--tions have to be solved ——— perhaps not too serious for the He sequence where the total number of equations to be solved is only four but for many-electron atoms the dimensionality of the problem rapidly becomes impossibly large.

2/ The alternative is to utilise the Aitken δ^2 process as described by Alexander and Gordon (A7) to find successive extrapolated vectors of the coupling terms, the method hopefully converging rapidly. In the process a new vector Q with elements Q(i) is defined after every three iterations of the simple scheme by the equation (38) where Q_1, Q_2, Q_3 are the vectors resulting from three successive cycles.*

$$Q(i) = Q_1(i) + (2Q_2(i) - Q_1(i) - Q_3(i))^{-1} (Q_2(i) - Q_1(i))^2 \qquad (38)$$

The formula (38) has been used frequently to attempt to improve the convergence rate in the determination of solutions of Roothaan's equations but for that topic the results of using the extrapolation process appears to be a matter of controversy (N1). For the problem

* N.B. in reference (A7) there appears to be a typographical error in the statement of (38).

investigated here though there is no doubt that it has a beneficial effect, yielding convergence when the simple iterative approach fails entirely in this respect. Before describing the results of the calcul--ations it may finally be noted that a first order damping formula (39) can also be used for evaluating successive vectors Q, λ being a factor between 0.0 and 1.0.

$$Q(i) = Q_1(i) + \lambda Q_2(i) \qquad (39)$$

Using the above it was found that convergence was accelerated when the simple scheme only slowly approached the limit but when the latter gave divergence (39) did not rectify the situation. Hence the use of (38) is generally desirable despite its somewhat greater complexity.

B Results for the dynamic polarisabilities in the SCF approaches.

Calculations of the frequency-dependent polarisability of a number of two-electron systems were carried out using the various methods related above and in Table 5.9 are listed the DUHF, uncoupled Hartree and CPHF $\alpha(\omega)$ for He for a wide range of frequencies which extend well into the region of anomalous dispersion. The results are believed to be accurate within the limitations imposed by the quality of the unperturbed orbitals, this being confirmed by the excellent agreement with the work of Alexander and Gordon (A6) in Table 5.10 for the uncoupled Hartree approximation.(The slight differences at high frequencies are probably due to the marginally more accurate represent--ation of the zeroth function adopted by Alexander and Gordon, the

Table 5.9 A comparison of values of the frequency-dependent polarisability of He within the DUHF, uncoupled Hartree and CPHF approximations.

ω	DUHF	Uncoupled Hartree	CPHF	Accurate[a]
0.0	0.99722	1.4871	1.3222	1.384
0.1	1.0024	1.5040	1.3363	1.399
0.2	1.0183	1.5577	1.3806	1.448
0.3	1.0462	1.6581	1.4629	1.541
0.4	1.0887	1.8275	1.6007	1.698
0.5	1.1502	2.1190	1.8342	1.971
0.6	1.2388	2.6862	2.2759	2.509
0.7	1.3708	4.2742	3.4344	4.119
0.75	—	7.4950	5.4852	7.969
0.79	—	390.46	25.211	-30.748
0.80	1.5849	-19.093	-49.668	-10.330
0.82	1.6456	-3.3973	-3.5894	—
0.84	1.7160	0.98831	0.74245	—
0.86	1.7996	31.781	12.088	—
0.88	1.9020	1.8462	1.4100	—
0.90	2.0352	-3.0372	-3.2391	—

[a] Elaborate calculation based on correlated wavefunction by Chung (C4) which is in good agreement with the experimental results of Cuthbertson & Cuthbertson (C12).

Table 5.10 A comparison of values for the frequency-dependent polarisability of He using the uncoupled Hartree approach.

ω	This work[a]	This work[b]	Alexander & Gordon[c]
0.0	1.4867	1.4871	1.4871
0.2	1.5573	1.5577	1.5577
0.4	1.8270	1.8275	1.8275
0.6	2.6861	2.6862	2.6863
0.7	4.2768	4.2742	4.2748
0.75	7.5089	7.4950	7.4985
0.79	408.89	390.46	——
0.80	-19.153	-19.093	-19.062
0.81	-7.4790	-7.4292	-7.4209
0.82	-3.4418	-3.3973	-3.3920
0.83	-1.0839	-1.0397	-1.0346
0.84	0.93898	0.98831	0.99490
0.85	3.9262	3.9927	4.0058
0.86	31.691	31.781	32.059
0.87	-4.0709	-4.1103	-4.1085
0.88	1.8281	1.8462	——
0.89	-3.9827	-4.0377	——
0.90	-2.9819	-3.0372	——

[a,b] Calculated from Clementi 4 and 5 term basis sets respectively.

[c] Reference (A6).

sensitivity of the $\alpha(\omega)$ to this factor being conspicuous from the quite substantial differences arising from the use of a 4 or 5 term basis set as seen in the Table.).

For He, as is known, the DUHF results are very poor owing to the form of the Hartree-Fock operator for which in general all the excited states lie in the continuum (K7, K8, L8). The uncoupled Hartree and CPHF results however both give a reasonable representation of the variation of α with ω at least as far as the start of the region of anomalous dispersion as may be observed from the comparison of the pre--sent work with the very accurate calculations of Chung (C4) which are in good agreement with the experimental refractive index data of Cuthbertson and Cuthbertson (C12). Indeed an interesting feature is that for $\omega > 0.5$ a.u. the uncoupled method is apparently superior to the coupled scheme, this being merely enhanced by the scaling of the $\alpha(\omega)$ to the correct static polarisability e.g. scaling gives for $\omega = 0.5$ a.u. 1.920 a.u. for the CPHF result and 1.972 a.u. for the uncoupled Hartree value in excellent, though somewhat fortuitous, agreement with the accurate dynamic polarisability.

For Li^+, for which detailed results are given in Table 5.11, unfortunately no accurate theoretical or experimental data appears to have been reported other than for $\omega = 0.0$.* It is though possible to compare the values of the poles in the region of anomalous dispersion for He or Li^+ with the experimental transition frequencies for the excitations $1s^2\ {}^1S \rightarrow 1snp\ {}^1P$, this being done in Table 5.12 in which previous theoretical results are also included. It can be seen that for

* "Accurate theoretical" meaning in this case a more refined calculation than one of the SCF approaches.

Table 5.11 A comparison of values for the frequency-dependent polarisability of Li^+ within the uncoupled Hartree and CPHF approximations.

ω	Uncoupled Hartree	CPHF	Variational CPHF[a]
0.0	0.20491	0.18948	0.1870
0.1	0.20521	0.18975	0.1873
0.5	0.21270	0.19632	0.1938
1.0	0.24077	0.22076	0.2178
1.5	0.31378	0.28311	—
2.0	0.61882	0.52665	0.5180
2.10	0.85739	0.70026	0.6882
2.20	1.6234	1.1769	1.1552
2.25	3.6261	2.0362	—
2.27	8.3228	3.0594	—
2.28	27.235	4.1867	—
2.29	-19.566	6.8383	6.6993
2.30	-6.9548	20.675	20.236
2.31	-4.1293	-18.005	-17.652

[a] Reference (M9).

Table 5.12 A comparison of values for the resonant frequencies of He and Li^+ within the arbitrary ranges 0.0 - 0.9 a.u. and 0.0 - 2.7 a.u. respectively. Calculations are executed within the uncoupled Hartree and CPHF approximations.

Excited state	Experimental[a]	Hartree[b]	CPHF	Numerical[c]	Variational[d]	Variational[e]
He						
$1s2p\,^1P$	0.780	0.7905	0.7970	0.79697	0.8020	0.797
$1s3p\,^1P$	0.849	0.8616	0.8636	0.86361	0.9942	0.863
$1s4p\,^1P$	0.873	0.8864	0.8872	0.88722	1.477	0.887
$1s5p\,^1P$	0.884	0.8978	0.8982	0.89822	2.853	0.898
Li^+						
$1s2p\,^1P$	2.286	2.284	2.305	-	-	2.304
$1s3p\,^1P$	2.559	2.567	2.574	-	-	2.573
$1s4p\,^1P$	2.656	2.666	2.669	-	-	2.669

[a] See reference (M7). [b] This work. [c] CPHF calculation of Alexander & Gordon (A7).

[d,e] Variational CPHF calculations of Dalgarno & Victor (D7) and Mukherjee, Sengupta & Mukherji (M9) respectively.

both systems the uncoupled Hartree method gives somewhat better values for the excitation energies than the CPHF approach although the differences decrease with n, both schemes converging smoothly on a sequence of frequencies which are somewhat in excess of the experimental results presumably due to correlation effects. With reference to this it may be remarked that for other spectral properties e.g. oscillator strengths, computed from CPHF and uncoupled Hartree calculations it has been shown by Jamieson (J1) that the coupled method generally gives more satisfactory results. Thus the superiority of the Hartree approach as noted here is to some extent accidental though not entirely devoid of importance.

To sum up it may be said that it has been seen that simple finite-difference methods can be fairly easily extended to the evaluation of frequency-dependent polarisabilities. It should perhaps be admitted that the technique cannot be increased in accuracy in the region of the poles beyond that indicated by Table 5.12 without becoming excessively cumbersome and expensive. However as the numerical error in any of the resonant frequencies is approximately two or three orders of magnitude less than the difference between the SCF and experimental transition energies it is felt that the present approach is more than adequate for this type of problem.

5.6 The calculation of polarisabilities for the Be isoelectronic sequence.

As noted in the Introduction to this Chapter the solution of the CPHF equations for atomic systems becomes rapidly extremely difficult as the number of electrons increases. It is thus important to

discover reliable approximations to the coupled method so that accurate, non-empirical evaluations of polarisabilities can be performed for medium and large atoms. Unfortunately although several such schemes have been previously proposed it is not easy to judge their accuracy owing to rather wide error margins on the results of various workers due to computational uncertainty. In this section two schemes will be exam--ined using the numerical techniques described in this Chapter with the objective of giving an unequivocal assessment of their ability to simulate successfully the fully coupled method.

A Theory and methods of solution

Consider the CPHF equations which have been previously given as (7). Clearly the equation for each perturbed orbital contains a plethora of terms which gives coupling to each of the other χ' and thus it may be anticipated that other than for a two-electron system the determination of the first order function would be an arduous task. For a four-electron atom it is though fairly easy to see a possible approximation to (7) which might be expected to be accurate:- The coupling terms are of two types viz. intrashell and intershell contri--butions with the latter being probably unimportant when one considers the magnitude of other intershell effects e.g. intershell correlation discussed in Chapter 3. Hence neglecting these cross-terms but retaining the intrashell consistency term which allows coupling between the two orbitals of opposite spin in each shell a Simplified Coupled Perturbed Hartree-Fock (SCPHF) method is obtained as (40).

$$\left(-\tfrac{1}{2}\nabla_1^2 - Z/r_1 + \sum_{i \neq j} \left\langle \chi_i^\circ \left| r_{12}^{-1}(2 - P_{12}) \right| \chi_i^\circ \right\rangle - \varepsilon_j^\circ \right.$$
$$\left. + \left\langle \chi_j^\circ \left| r_{12}^{-1}(1 + P_{12}) \right| \underline{\chi}_j^\circ \right\rangle \right) \chi_j^1(1)$$
$$= \left(\varepsilon_j^1 - h'(1) \right) \chi_j^\circ(1) \qquad (40)$$

The above is the method b of Langhoff, Karplus and Hurst (L4) and, as noted by these authors, the field due to the electrons acting on each perturbed orbital χ_n^1 is $2J_{n'} - K_{n'}$ for $n' \neq n$ and $J_{n'} + 2K_{n'}$ for $n' = n$. The equations (40) can be straightforwardly reduced to radial form, it being found that it is required to solve an equation (41) for each shell, this being only a little more complex than (10).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} - Z/r + 2J_{n's}(r) + J_{ns}(r) - K_{n's}(r) \right.$$
$$\left. + 2K_{ns}(r) - \varepsilon_{ns}^\circ \right) f_{ns}(r) = -r^\ell P_{ns}(r) \qquad (41)$$

The other scheme which was chosen for examination is the DUHF approach previously discussed for two-electron atoms. For the Be sequence it is again only required to solve two equations, these being provided by (42).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} - Z/r + 2J_{n's}(r) + 2J_{ns}(r) \right.$$
$$\left. - K_{n's}(r) - K_{ns}(r) - \varepsilon_{ns}^\circ \right) f_{ns}(r) = -r^\ell P_{ns}(r) \qquad (42)$$

Owing to the spurious self-potential term on the L.H.S. of (41) it has been found that poor results are obtained when a_o is calculated direct--ly from the solutions of (42) (L4, E1). As before though, the first order correction (43) can be evaluated from only the χ^1 as has been shown by Tuan, Epstein and Hirschfelder (T3) by the use of double perturbation theory.

$$a_1 = -\sum_{i=1}^{N}\sum_{j=1}^{N} (\langle i^1 j^1 | i^o j^o \rangle + \langle i^o j^o | i^1 j^1 \rangle + 2\langle i^1 j^o | i^o j^1 \rangle - \langle i^1 j^1 | j^o i^o \rangle - \langle i^1 j^1 | j^o i^o \rangle - 2\langle i^1 j^o | j^1 i^o \rangle) \qquad (43)$$

where

$$\langle i^a j^b | k^c l^d \rangle = \int \chi_i^a(1)\, \chi_j^b(2)\, r_{12}^{-1}\, \chi_k^c(1)\, \chi_l^d(2)\, d\tau_1\, d\tau_2 \qquad (44)$$

The explicit form of (43) for the Be series is (45) (in similar notation to (44) but with the integrations over spin completed, μ representing the space part of the requisite orbital). This expression can be seen to contain only integrals of a type already dealt with.

$$\begin{aligned} a_1 = {} & 4\langle \mu_{1s}^1 \mu_{1s}^o | \mu_{1s}^1 \mu_{1s}^o \rangle - 12\langle \mu_{1s}^1 \mu_{1s}^1 | \mu_{1s}^o \mu_{1s}^o \rangle + \\ & 4\langle \mu_{2s}^1 \mu_{2s}^o | \mu_{2s}^1 \mu_{2s}^o \rangle - 12\langle \mu_{2s}^1 \mu_{2s}^1 | \mu_{2s}^o \mu_{2s}^o \rangle - \\ & 32\langle \mu_{1s}^1 \mu_{2s}^1 | \mu_{1s}^o \mu_{2s}^o \rangle + 8\langle \mu_{1s}^1 \mu_{2s}^1 | \mu_{2s}^o \mu_{1s}^o \rangle + \\ & 8\langle \mu_{1s}^1 \mu_{1s}^o | \mu_{2s}^1 \mu_{2s}^o \rangle \end{aligned} \qquad (45)$$

Hence, with little difficulty, the DUHF values can be greatly improved as will be seen in the discussion.

Finally it is easy to see that both schemes can be extended to the frequency-dependent case but it was not considered worthwhile to investigate further the second of these owing to its qualitatively incorrect behaviour noted previously for the two-electron sequence and confirmed for Be by Levine and Taylor (L8). However no previous calcul--ations of the dynamic polarisability of any many-electron system appear to have been reported using the SCPHF method and hence it is of interest to pursue this approach a little further. Following a similar reduction as was carried out for the static problem, (30) yields in the SCPHF approximation the two pairs of radiall equations (46) which are obviously akin to (34).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\,r^{-2} - Z/r + 2J_{n's}(r) + J_{ns}(r) - \varepsilon^{o}_{ns} \pm \omega \right) f^{\pm}_{\ell}(r) = -\left(r^{\ell} P_{ns}(r) - K_{n's} f^{\pm}_{ns}(r) + K_{ns} f^{+}_{ns}(r) + K_{ns} f^{-}_{ns}(r) \right) \qquad (46)$$

To solve the various equations for the perturbed orbitals presented in this section the techniques employed for the two-electron sequence were applied without difficulty. It was found though to be economical to use the Aitken δ^2 process given as formula (38) quite generally to accelerate the convergence of the iterative scheme necessitated by the non-local terms appearing in the inhomogeneity of each radial equation.

B Discussion of results for the Be sequence

Extensive calculations of the dipole and quadrupole polar-isabilities of the members of the beryllium isoelectronic sequence were performed using the SCPHF and DUHF approximations employing the analytic zeroth functions listed by Clementi (C7).

In Tables 5.13 and 5.14 the SCPHF results for the dipole and quadrupole polarisabilities are compared with the values of other workers derived from various Coupled Hartree-Fock procedures and it can be observed that excellent agreement is maintained between the present work and previous accurate studies. The dipole polarisabilities related by Langhoff, Karplus and Hurst (L4) are however exceptional but this is probably a consequence of the rather restrictive form of the variational trial function utilised by these researchers.* Interestingly the quadrupole polarisabilities do not appear to show this effect..... This is possibly a result of the increased importance of the outer parts of the zeroth functions for this set of calculations (see for Be in the increased sensitivity of the 2^{ℓ} polarisability to the quality of the unperturbed orbitals as ℓ increases) and hence the constraint of rigidly preserving the node in the 2s first order function as detailed by Langhoff et al is probably less severe than for the dipole polarisability studies.

From the above it may be concluded that the SCPHF method is a valid approximation to the fully coupled scheme for the systems

* The conclusion by Tuan and Davidz (T2) that the SCPHF method is not particularly satisfactory for the Be sequence on the basis of a compar-ison of the results of Langhoff et al with other CPHF calculations is probably erroneous for similar reasons.

Table 5.13 A comparison of the present SCPHF results with previous values of the dipole polarisabilities of the systems Li^- — Ne^{6+} derived from various CHF procedures.

	This work[a]	This work	Cohen[b]		Other		
Li^-	1182.8	1183.0	1050.				
Be[c]	45.513	45.566	45.5	45.61[e]	45.60_9[f]	42.2[g]	42.1
Be[d]	45.569	45.622					
B^+	11.379	11.398	11.35	11.38	11.37_4	9.45	9.45
C^{2+}	4.4998	4.5089	4.49	4.508	4.501_2	3.35	3.35
N^{3+}	2.2326	2.2373	2.22	2.237	2.233_9	1.49	1.50
O^{4+}	1.2686	1.2712	1.27	1.271	1.261_7	0.769	0.776
F^{5+}	0.78937	0.79101	0.784	0.7903	0.7884_5	0.439	0.441
Ne^{6+}	0.52437	0.52543	0.522	0.5251			

[a] Contribution of 2s shell to the polarisability. Next column gives the total value of the polarisability.

[b] Reference (C8). Cerived from non-perturbative CHF procedure.

[c,d] Results obtained using 6 and 5 term zeroth functions respectively.

[e,f] CPHF results of Lahiri and Mukherji (L1) and of Tuan and Davidz (T2) respectively.

[g] Results of Langhoff, Karplus and Hurst (L4) obtained using a rather restrictive form of variational trial function. The first column gives CPHF values, the second those from an SCPHF calculation.

Table 5.14 A comparison of the present SCPHF results with previous values of the quadrupole polarisabilities of the systems Li^- — Ne^{6+} derived from various CHF procedures.

	This work[a]	This work	Other	
Li^-	1.0975×10^5	1.0975×10^5		
Be[b]	342.56	342.57	342.5[d]	347[e]
Be[c]	344.98	345.00		
B^+	28.683	28.686	28.27	28.9
C^{2+}	5.2498	5.2509	5.225	5.23
N^{3+}	1.4367	1.4371	1.433	1.43
O^{4+}	0.50093	0.50110	0.4996	0.499
F^{5+}	0.20558	0.20566	0.2048	0.204
Ne^{6+}	0.094920	0.094960	0.09460	

[a] Contribution of the 2s shell to the polarisability. Next column gives the total value of the polarisability.

[b,c] Computed from 6 and 5 term zeroth functions respectively.

[d] CPHF results of Lahiri and Mukherji (L2).

[e] Identical CPHF and SCPHF results of Langhoff, Karplus and Hurst (L4).

under investigation, the two approaches giving negligibly different values for the static multipole polarisabilities. In addition for Be the present dipole and quadrupole polarisabilities of 45.566 and 342.57 a.u. are in harmony with the results of Kelly (K8), obtained from many-body perturbation theory, of 46.8 and 340. a.u. which are expected to be close to the exact values. It should not though be denied that there is some uncertainty over the true values of the polarisabilities of the members of the Be sequence due to the obfuscating factor of the $2s^2$ — $2p^2$ near-degeneracy effect discussed in Chapter 3. Attempting to allow for this by the use of a CI method, Kolker and Michels (K13) obtained a dipole polarisability of 37.1 a.u. for Be which is substan--tially lower than the others given here. As far as the author is aware this discrepancy between the different α is still unresolved in the absence of sufficient accurate theoretical or experimental data.

Before leaving the discussion of the SCPHF results it may be remarked that the 1s shell contributes little to the polarisability* and the computation time for each calculation could be halved without probably introducing any greater errors than are involved in initially approximating the coupled method with the simplified scheme. Two rather obvious implications for extending polarisability calculations to larger atomic systems flow from this:- Firstly if two atomic shells are sufficiently separated that the SCPHF method is a good approximation to the CPHF approach then it is also likely that it will be valid to neglect the contribution of the inner shell(s) to α entirely. Secondly the

* Comparison of the 1s shell contribution to each SCPHF polarisability for the four-electron sequence with the corresponding CPHF value for the He series in Table 5.1 shows these to be almost identical as might be expected.

small magnitude of the 1s shell polarisability can be viewed as a partial justification of semi-empirical calculations in which the polarisability of an atom is evaluated from only the contributions of the valence 'electrons', the effect of the core appearing only as a pseudopotential in H^{o}. This question will be further discussed in Chapter 7.

In Tables 5.15 and 5.16 the DUHF dipole and quadrupole polarisabilities for the Be sequence are related, geometrically approxi-mated values defined as earlier in the Chapter being also included. The present work confirms the fact that whereas the DUHF a_0 are generally too small in comparison to the probable exact polarisabilities when the first order corrections are included the situation is greatly improved (E1). Of particular interest is the geometric approximation as the efficacy of this formula is not entirely clear for four-electron systems. For the dipole polarisabilities assuming, as seems likely, that the SCPHF results are close to the true CPHF values it can be seen that the geometric approximation gives a shortfall of about the 2% found by Tuan and Davidz (T2) in accurate variational calculations.* This is however very satisfactory considering the much larger errors in a_0 and $a_0 + a_1$. For example for Be the error in the former is about 33% and in the latter about 12% of the CPHF value. For the quadrupole polarisabilities though, as was seen for the two-electron series as ℓ was increased, the geometric relationship appears to be even more accurate with an

* Further accurate calculations are required on other systems to establish if this slightly larger error for the Be sequence than for the He series is a result of a gradual diminution of the accuracy of the geometric approximation as the number of electrons in the system is increased or whether it is a peculiarity of these systems due to near-degeneracy as proposed by Tuan (T1).

Table 5.15 The DUHF results for the dipole polarisability of the mem-bers of the beryllium isoelectronic sequence.

	a_o	a_1	$a_o + a_1$	Geometric approx.
Li^-	0.50185(3)	0.26469(3)	0.76653(3)	0.10619(4)
Be[a]	0.30556(2)	0.97199(1)	0.40275(2)	0.44810(2)
Be[b]	0.30587(2)	0.97336(1)	0.40321(2)	0.44864(2)
B^+	0.81642(1)	0.22212(1)	0.10385(2)	0.11216(2)
C^{2+}	0.32879(1)	0.84200(0)	0.41299(1)	0.44197(1)
N^{3+}	0.16372(1)	0.41098(0)	0.20482(1)	0.21859(1)
O^{4+}	0.92864(0)	0.23272(0)	0.11614(1)	0.12392(1)
F^{5+}	0.57566(0)	0.14524(0)	0.72090(0)	0.76991(0)
Ne^{6+}	0.38066(0)	0.97068(-1)	0.47773(0)	0.51095(0)

[a] Computed using 6 term zeroth function.

[b] Computed using 5 term zeroth function.

Table 5.16 The DUHF results for the quadrupole polarisability of the members of the beryllium isoelectronic sequence.

	a_o	a_1	$a_o + a_1$	Geometric approx.
Li^-	0.40087(5)	0.25325(5)	0.65412(5)	0.10886(6)
Be^a	0.22044(3)	0.78545(2)	0.29898(3)	0.34246(3)
Be^b	0.22201(3)	0.79094(2)	0.30110(3)	0.34488(3)
B^+	0.21102(2)	0.55752(1)	0.26677(2)	0.28679(2)
C^{2+}	0.41321(1)	0.87953(0)	0.50116(1)	0.52495(1)
N^{3+}	0.11794(1)	0.21120(0)	0.13906(1)	0.14367(1)
O^{4+}	0.42338(0)	0.65568(-1)	0.48894(0)	0.50096(0)
F^{5+}	0.17752(0)	0.24250(-1)	0.20177(0)	0.20560(0)
Ne^{6+}	0.83326(-1)	0.10190(-1)	0.93516(-1)	0.94935(-1)

[a] Computed using 6 term zeroth function.

[b] Computed using 5 term zeroth function.

inconsequential difference of only 1 part in 3000 between the SCPHF and geometrically approximated DUHF polarisabilities even though the errors in a_o and $a_o + a_1$ are by no means small e.g. about 36 and 13% for Be. Again also the interesting effect by which various schemes converge to the same final polarisability if the same zeroth function (even if this is somewhat inaccurate) is employed for all calculations is observed in the two sets of values for the quadrupole polarisability of Be.

It may thus be concluded that either the SCPHF or the DUHF scheme yields polarisabilities for the Be sequence which are good approximations to the true CPHF values. As far as the computational effort is concerned there is little to choose between the two methods, the slightly faster convergence of the DUHF approach being counterbalan--ced by the need to evaluate the first order correction to a_o. For larger systems it is unfortunately not possible at this time to make an a priori judgement of the possible merits of each method as there are too many factors of which little is known or which require confirmation by explicit calculation e.g. for Ne it would seem quite likely that the SCPHF approach would yield poor results as the 2s/2p coupling terms are probably not small since the unperturbed orbitals occupy approximately the same region in space (cf. the values of the 1s2s, 1s2p and 2s2p pair correlation energies in Ne (V3)).

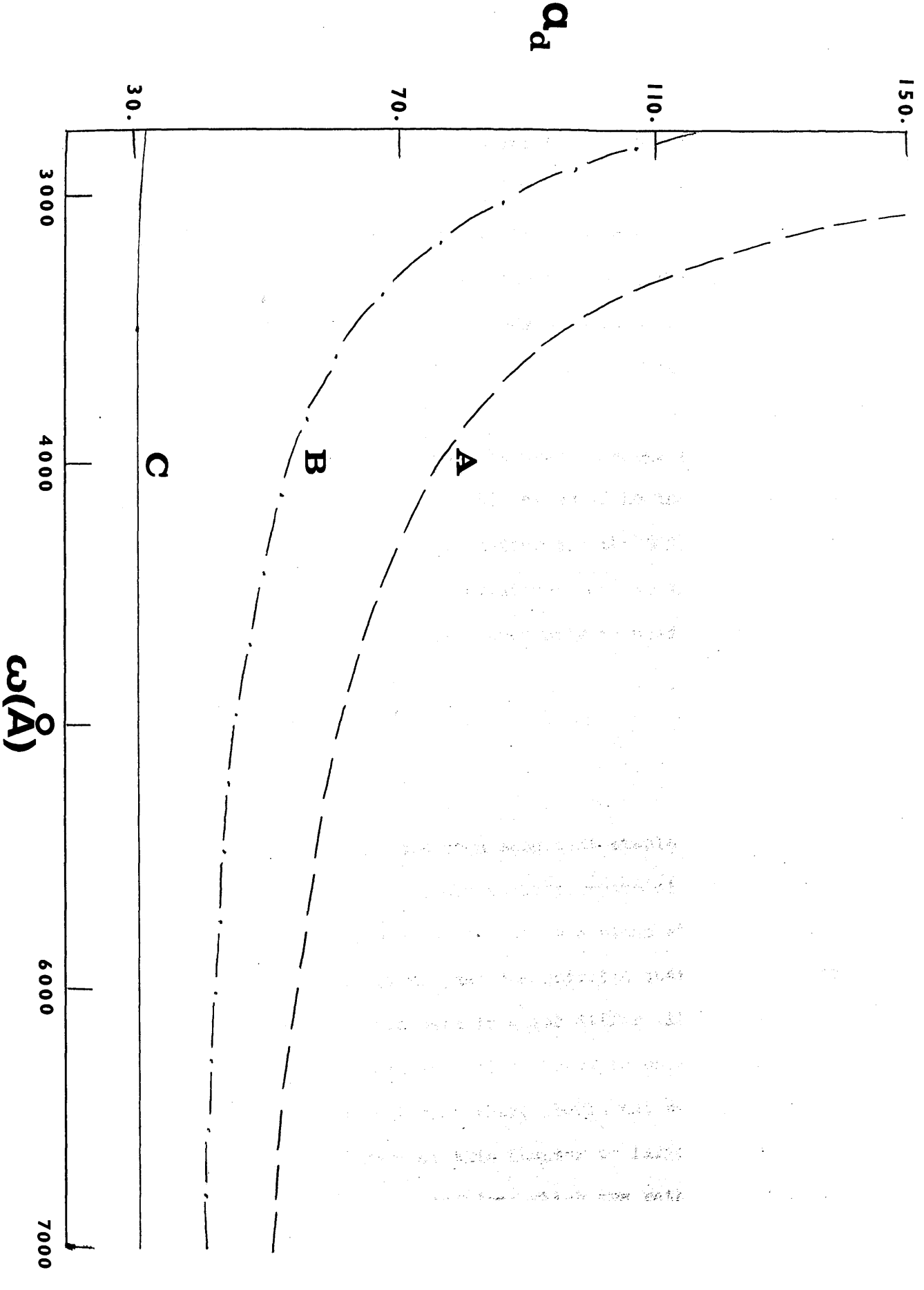
Lastly the extension to the frequency-dependent case can be considered. In Table 5.17 SCPHF dynamic polarisabilities for Be are listed for a wide range of frequencies together with the variational fully coupled results of Kaveeshwar, Chung and Hurst (K6). Again the SCPHF and CPHF values appear to be in very good agreement though near the pole corresponding to the $1s^2 2s^2\ ^1S \rightarrow 1s^2 2s2p\ ^1P$ transition the dispar--ity becomes somewhat larger though it is not clear whether this is due

Table 5.17 A comparison of the SCPHF results for the frequency-dependent polarisability of Be with the values obtained by Kaveeshwar, Chung and Hurst (K6) from fully coupled CPHF calculations.

Wavelength (Å)	This work	Kaveeshwar et al
∞	45.566	45.624
20000.0	46.316	—
9071.0	49.463	49.538
8063.0	50.616	50.694
7257.0	51.969	52.053
6047.0	55.409	55.500
5183.0	60.123	60.216
4535.0	66.688	66.770
4032.0	76.117	76.191
3628.0	90.542	90.479
3456.0	100.82	100.679
3299.0	114.54	114.196
3155.0	133.73	132.888
3024.0	161.94	160.330
2903.0	208.04	204.394
2791.0	296.46	286.436
2688.0	521.05	491.938
2650.0	754.56	—
2600.0	1983.7	—
2592.0	2727.7	1933.777
2550.0	-2645.3	—
2502.0	-789.03	-946.774
2500.0	-765.75	—
2400.0	-294.26	—

Figure 5.2

A comparison for the dynamic dipole polarisability of Be of the present SCPHF work, the CI results of Kolker and Michels (K13) and the DUHF values of Levine and Taylor (L8), (Curves A, B and C respectively). The polarisabilities are given in a.u. though the incident radiation wavelength is in Ångstroms.


α_d
30.
70.
110.
150.
3000
4000
6000
7000
$\omega(\mathring{A})$
A
B
C

to the approximations involved in the SCPHF method or some other reason e.g. the use of different unperturbed orbitals (see Addendum). The computed resonance is however also in harmony with that from the fully coupled calculation being estimated at 2570 Å in comparison to the 2592 Å of Kaveeshwar et al, both results being somewhat in error when the experimental value of 2349 Å is considered. The SCF excitation energies are also inferior to the many-body perturbation theory value of this quantity of Kelly (K8) which, at 2355 Å, differs only margin--ally from experiment. Finally from Figure 5.2 it can be observed that there are decided differences betwenn the present work, the CI results of Kolker and Michels (K13) and the DUHF values of Levine and Taylor (L8). The reasons for the unsatisfactory behaviour for the DUHF scheme have already been discussed but the CI calculations, as for the static polarisability computation, are still apparently in need of explanation.

5.7 Conclusions

In this Chapter it has been seen that simple finite-difference techniques provide a highly accurate means of calculating the multipole polarisabilities of small atomic systems within various levels of theory. Notably their use has demonstrated that approximations such as the SCPHF method do give results which differ little from those from the CPHF approach, at least in certain specific cases and possibly more generally. Hence it is felt that there should not be any great difficulty in extending the work of this Chapter to larger atoms although it will be necessary to solve new problems which are rather similar to those discussed at the end of Chapter 3 in connection with the further development of electron pair correlation research e.g. the problem of

the maintenance of orthogonality among the perturbed/unperturbed orbitals. These difficulties are however intrinsically less awkward to handle than those examined in 3 and fairly rapid progress should be possible. In particular the DUHF scheme with the application of the geometric approximation, assuming the general validity of the latter,* seems a promising approach to the non-empirical calculation of atomic polarisabilities since the computational labour rises much less sharply than for the fully coupled method.

The procedures dealt with here are though not confined in scope to the determination of polarisabilities and hence for other effects which result from the perturbation of an atomic system by a single-particle operator a similar approach is perhaps appropriate. In addition it should be possible to extend studies beyond first order in the wavefunction without the method becoming inaccurate. An interesting and important future application of this is the calculation of atomic hyperpolarisabilities, the recent article by Bhattacharya, Sengupta and Mukherji (B9) emphasising the need for an accurate theoretical treatment of this problem to attempt to resolve the discrepancies between the theoretical and experimental results of various workers. Such a project, on the lines of the work of this Chapter, has been initiated.

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* Some DUHF computations on the Ne isoelectronic sequence by Tuan and Wu support the suggestion that the geometric approximation is widely applicable for this type of calculation. See references (T1, T5).

Chapter 6 A Finite-Difference Approach to Long-Range Interactions: Non-Empirical Methods.

6.1 Introduction

Numerous studies have been carried out upon long-range interactions between atoms employing diverse methods of calculation. No attempt will however be made to review the latter here and the reader is referred to the comprehensive and lucid articles by Dalgarno (D1) and Dalgarno and Davison (D2). Nevertheless despite the considerable interest in this topic it does not appear to have been previously suggested that finite-difference techniques may provide a highly accurate means of determining the various coefficients $\sum_n B_n R^{-n}$ of the interaction energy.* In this Chapter it is intended to demonstrate that simple numerical methods yield a most powerful and elegant tool for the determination of these quantities.

In the first part of this section of the thesis the method will be extensively investigated for the H — H system for which a number of other accurate calculations are available for the purposes of

* Van der waals coefficients could also be determined from the work of Chapter 5 on frequency-dependent polarisabilities using a one-centre formalism (III C in the review of Dalgarno and Davison). The approach used in this Chapter is however considerably more efficient and accurate. It is also much more direct and, in the opinion of the author, gives a comprehensible and physically appealing picture of the processes involved which give attractive forces between atoms at long range.

comparison. Not only will the ground state interaction be dealt with but also the appropriate coefficients will be evaluated for the 1S2S and 1S2P states which are of importance in studies of the dissociation of the hydrogen molecule.

The second half of the Chapter will be concerned with the extension of the techniques used for H — H to the interaction of two-electron atoms and ions. As before a non-empirical theory, that of the uncoupled Hartree approach, is employed with the use of semi-empirical techniques in conjunction with these finite-difference methods being reserved until Chapter 8.

The theory for the interaction of two hydrogen atoms at long range, briefly mentioned in 1.3, will now be delineated.

6.2 Theory and numerical methods for the long-range interaction of two hydrogen atoms.

The Hamiltonian for the system may be written as:

$$H = H^{o} + H' \tag{1}$$

where

$$H^{o} = H(a1) + H(b2) \tag{2}$$

and

$$H' = \Sigma H'_{ij} = \Sigma 4\pi M_{ij} r_{a1}^{i} r_{b2}^{j} R^{-i-j-1} \theta_{ij} \tag{3}$$

Electron 1 is associated with nucleus a, electron 2 with b and the two nuclei are separated by R units. The M_{ij} and θ_{ij} are given by forms such as (4) and (5a), (5b), a full list being tabulated by Kolos (K14).

$$M_{11} = (2/3)^{-\frac{1}{2}}; \qquad M_{21} = 1 \tag{4}$$

$$\theta_{11} = 6^{-\frac{1}{2}}(Y_1^{-1}Y_1^{-1} + 2Y_1^0Y_1^0 + Y_1^1Y_1^1) \tag{5a}$$

$$\theta_{21} = 15^{-\frac{1}{2}}(3^{-\frac{1}{2}}Y_2^{-1}Y_1^{-1} + 3Y_2^0Y_1^0 + 3^{-\frac{1}{2}}Y_2^1Y_1^1) \tag{5b}$$

It is now desired to evaluate the interaction energy between the two atoms from the familiar first order perturbation equation (6).

$$(H^o - E0)\Psi' = (E1 - H')\Psi^o \tag{6}$$

At very large internuclear distances the overlap between orbitals on the different atomic centres is neglected and hence for the ground state the zeroth function can be written in simple product form. Similarly in the notation of Kolos a Ψ^o of the type (7) is assumed for the 1S2S excited states, the positive sign pertaining to the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states and the alternative to $^1\Sigma_u^+$ and $^3\Sigma_g^+$.

$$\Psi^o = 2^{-\frac{1}{2}}(1S2S \pm 2S1S) \tag{7}$$

Now the first order wavefunction must clearly be compounded of terms having the same angular dependence as H' and can be expanded as in (8).

$$\Psi = \sum U_{ij}(r_{a1}, r_{b2})\ \theta_{ij}\ R^{-i-j-1} \qquad (8)$$

Insertion of (8) into (6) yields a set of decoupled elliptic partial differential equations for the U_{ij} which have the general form (9) for the ground state interaction.

$$\left(-\tfrac{1}{2} \left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^{2} \frac{\partial}{\partial r_{a1}} \right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^{2} \frac{\partial}{\partial r_{b2}} \right) \right) + \tfrac{1}{2} \ell_i (\ell_i + 1)\ r_{a1}^{-2} \right.$$

$$\left. + \tfrac{1}{2} \ell_j (\ell_j + 1)\ r_{b2}^{-2} - r_{a1}^{-1} - r_{b2}^{-1} + 1.0 \right) U_{ij}(r_{a1}, r_{b2})$$

$$= -4.0\ M_{ij}\ r_{a1}^{i}\ r_{b2}^{j} \exp(-r_{a1}) \exp(-r_{b2}) \qquad (9)$$

The interaction is hence, to second order, expressible as the well-known series (10), the B_n being very simply found from the various solutions of (9) as in (11).

$$E2 = \sum_{n} B_n R^{-n} \qquad (10)$$

$$B_n = 4.0\ M_{ij} \int U_{ij}(r_{a1}, r_{b2})\ r_{a1}^{i+2}\ r_{b2}^{j+2} \exp(-r_{a1}) \exp(-r_{b2})\ dr_1 dr_2 \qquad (11)$$

For the 1S2S excited states the theory is little different from that for the 1S1S interaction and the relevant radial equations are:

$$\left(-\tfrac{1}{2}\left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^{2} \frac{\partial}{\partial r_{a1}}\right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^{2} \frac{\partial}{\partial r_{b2}}\right)\right) + \tfrac{1}{2} \ell_i(\ell_i + 1)\, r_{a1}^{2} \right.$$

$$\left. + \tfrac{1}{2} \ell_j(\ell_j + 1)\, r_{b2}^{-2} - r_{a1}^{-1} - r_{b2}^{-1} + 0.625 \right) U_{ij}(r_{a1}, r_{b2})$$

$$= 2^{-\frac{1}{2}} M_{ij}\, r_{a1}^{i}\, r_{b2}^{j} \left(R_{1s}(r_{a1})\, R_{2s}(r_{b2}) \pm R_{2s}(r_{a1})\, R_{1s}(r_{b2})\right) \qquad (12)$$

where R_{1s}, R_{2s} are normalised hydrogenic radial functions.

The treatment of the 1S2P states is somewhat more complicated. The unperturbed function is written as (13) for the Σ states, results for the Π states being expressible, as shown by Kolos, in terms of these.

$$\psi^{o} = 2^{-\frac{1}{2}} (1S2P\sigma \pm 2P\sigma 1S) \qquad (13)$$

This time there is a non-vanishing first order correction which goes as $B_3 R^{-3}$ where

$$B_3 = \pm (2^{16}/3^{10}) = \pm 1.1098579 \qquad (14)$$

Additionally the product of H' and ψ^{o} for these states gives angular components which are different from those in (5) e.g. H'_{21} furnishes θ_{22} and θ_{20} with these quantities defined as in (15a) and (15b).

$$\theta_{22} = 6^{-\frac{1}{2}}(Y_2^{-1}Y_2^{-1} + 2Y_2^{0}Y_2^{0} + Y_2^{1}Y_2^{1}) \qquad (15a)$$

$$\theta_{20} = Y_2^{0}Y_0^{0} \qquad (15b)$$

Overall though the application of perturbation theory leads to, after manipulation, a set of partial differential equations similar to those already discussed. Even the non-zero El only affects one portion of the R^{-6} or R^{-8} terms, this being the part having the angular dependence $Y_1^0 Y_0^0$ or $Y_0^0 Y_1^0$. Nevertheless (16) is readily furnished for U_{10} with an equivalent equation for U_{01}.

$$\left(-\tfrac{1}{2} \left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^2 \frac{\partial}{\partial r_{a1}} \right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^2 \frac{\partial}{\partial r_{b2}} \right) \right) + r_{a1}^{-2} \right.$$

$$\left. - r_{a1}^{-1} - r_{b2}^{-1} + 0.625 \right) U_{10}(r_{a1}, r_{b2})$$

$$= -2^{-\frac{1}{2}} \left(\tfrac{2}{3} R_{1s}(r_{a1}) R_{2p}(r_{b2}) r_{a1} r_{b2} - \mathrm{El}\, R_{2p}(r_{a1}) R_{1s}(r_{b2}) \right) \quad (16)$$

The equations which are required to be solved for the U_{ij} such as (9) are quite remarkably similar to those dealt with in Chapters 2 and 3 in which perturbation approaches to electron correlation in small atomic systems were studied. Thus programs which had been used for the electron pair calculations could be employed with only relatively small amendments for the evaluation of the B_n. A point to notice is that iterative methods can be utilised for the solution of the linear equations resulting on discretisation of the derivatives of the derivatives as the 'centrifugal' terms $\ell(\ell+1)/2r^2$ generally give diagonal dominance of the finite-difference matrix. For the ground state calculation the details of the computation have been described in 1.3. For excited states the only difference is the use of a more extended cutoff viz. 50.0 a.u. with the exception of the term B_{6b} (in the notation of Kolos) for the 1S2P states for which a cutoff of 40.0 a.u. is employed. For this pair function the finite-difference matrix is not as diagonally dominant as

for the other U_{ij} and this causes a little more difficulty. The result however is believed to be reliable agreeing excellently with that of Kolos.

6.3 Results for the long-range interaction of two hydrogen atoms

In Table 6.1 the coefficients B_6, B_8 and B_{10} obtained by numerical methods are compared with the variational results of Kolos (K14) and the essentially exact values calculated by Deal (D11), B_{10} being partitioned, as is customary, into dipole-octupole and quadrupole-quadrupole contributions B_{10}^1 and B_{10}^2. It is apparent that the results for the ground state interaction are of eight to nine figure accuracy which is likely to be more than sufficient for most purposes.

In treating the excited states 1S2S Kolos found that in order to achieve convergence for the B_8 coefficient it was necessary to employ a considerably larger set of basis functions than for the ground state computation. Table 6.2 contains the results of the numerical calcula-tions for these states and it can be observed that the B_6 coefficients are in accord with those obtained by that author whilst for B_8 the insufficiency of even the enlarged basis is apparent, the variational values correctly being higher than their numerical counterparts. The B_{10} coefficient is evaluated for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states to be $-2509676._6$ which is comprised of a dipole-octupole contribution of $-2201375._2$ and a quadrupole-quadrupole term of -308301.4. For the $^1\Sigma_u^+$ and $^3\Sigma_g^+$ states the B_{10} of $-2305530._0$ is compounded of a B_{10}^1 and B_{10}^2 of $-2077542._6$ and -227987.4 respectively.

It is hence not surprising to note, considering the large magnitude of the B_{10} given above, that the higher order terms B_8 and

Table 6.1 A comparison of the coefficients in the long-range interaction energy expansion for the ground state of the hydrogen molecule.

	Kolos (K14)	This work	Deal (D11)
B_6	-6.499027	-6.4990266_5	-6.4990267054_0
B_8	-124.3991	-124.39908_3	-124.399083583_5
B_{10}^1	-2150.614	-2150.6143_7	-2150.61437506_4
B_{10}^2	-1135.214	-1135.2140_4	-1135.21403989_7
$B_{10}^1 + B_{10}^2$	-3285.828	-3285.8284_1	-3285.82841496_1

[1] Dipole-octupole term.

[2] Quadrupole-quadrupole term.

Table 6.2 The values of the B_n coefficients for the long-range interaction of two hydrogen atoms in 1S2S states.

	This work	Kolos
$^1\Sigma_g^+,\ ^3\Sigma_u^+$		
B_6	-204.7355_1	-204.736
B_8	-19589.08_5	-19588.6
B_{10}^1	$-2201375._2$	—
B_{10}^2	-308301.3_6	—
$B_{10}^1 + B_{10}^2$	$-2509676._6$	—

	This work	Kolos
$^1\Sigma_u^+,\ ^3\Sigma_g^+$		
B_6	-148.7690_2	-148.769
B_8	-16607.73_5	-16607.2
B_{10}^1	$-2077543._6$	—
B_{10}^2	-227987.4_4	—
$B_{10}^1 + B_{10}^2$	$-2305531._0$	—

[1] Dipole–octupole term.

[2] Quadrupole–quadrupole term.

B_{10} make a significant contribution to the second order interaction energy even to very large interatomic separation. For example for the $^1\Sigma_u^+$ state, a case quoted by Kolos, at 10 a.u. the B_8 and B_{10} terms account for 72.72% of the interaction energy and even at 20 a.u. their contribu-tion is still appreciable at 27.32%. The omission of such terms clearly will result in a noticeable depletion in accuracy particularly at internuclear distances below 20.0 a.u., although for an interatomic separation as small as 10 a.u. overlap effects, which are neglected here, are of major importance (K14, M10).

Finally in Table 6.3 the various contributions to the B_6 and B_8 coefficients are listed for the 1S2P states, the notation of Kolos being followed for the indexing of these quantities. For six of the terms excellent agreement is again found with Kolos to the seven figures given by him. For another, as previously mentioned, the numerical value is not determined to the precision of the other terms owing to some small computational difficulties. Nevertheless the previous and present values are still in accord with the finite-difference results lying marginally lower as would be expected as slow convergence is again apparent in the variational calculation. The same situation unfortunately does not prevail for the contribution B_{8d} for which there is a considerable discrepancy between the two values. No explanation can be offered for this at present though it is unlikely to be due to numerical instability as calculations on both linear and 'square root' grids with varying cutoffs and numbers of grid points all gave about the same value for the coefficient. The effect of this possible error is however not serious for the purposes of evaluating the second order energy from the power series (10) at reasonable internuclear distances e.g. at 20.0 a.u. B_6R^{-6} + B_8R^{-8} is changed by less than 2% for the 1S2P Σ states using the numerical value for B_{8d} in place of the variational result, this being

Table 6.3 The values of the B_n coefficients for the long-range interaction of two hydrogen atoms in 1S2P Σ states. The coefficients are identical for the $^1\Sigma_g^+$, $^3\Sigma_u^+$ and the $^1\Sigma_u^+$, $^3\Sigma_g^+$ states unless otherwise indicated.

	$^1\Sigma_g^+$, $^3\Sigma_u^+$		$^1\Sigma_u^+$, $^3\Sigma_g^+$	
	This work	Kolos	This work	Kolos
B_{6a}	-82.97414_7	-82.9741	—	—
B_{6b}	-91.193[a]	-91.1916	—	—
B_{8a}	-6487.834_9	-6487.83	—	—
B_{8b}	-8494.472_9	-8494.473	-6674.400_3	-6674.40
B_{8c}	-1061.967_6	-1061.968	-353.1689_9	-353.169
B_{8d}	-770.4383_8	-2265.48	—	—

[a] This coefficient is not determined to the same accuracy as the others.

insignificant in comparison to the neglect of overlap effects, higher order terms and so on.* Thus the deductions of Kolos for the various states from his computed values of the B_n are not materially affected by this work.

In conclusion it can be said that finite-difference techniques provide an efficient means of evaluating the long-range interaction energy between atoms. The method is admittedly surpassed in accuracy for the ground state of H_2 by the work of Deal (D11) but it must be observed that this is a tour de force which cannot be readily extended to other systems. On the contrary the numerical approach is quite general as will be seen in the next section in which the interaction of two-electron atoms and ions will be examined.

6.4 Interaction of two-electron atoms and ions in the uncoupled Hartree approach

A Theory and method of calculation

For the interaction of a pair of two-electron atoms in the uncoupled Hartree approach the zeroth wavefunction is of simple product form with, for the sub-systems a and b, each orbital satisfying an

* Unfortunately for the 1S2P states higher order terms than B_8 cannot be evaluated conveniently owing to two factors:- Firstly the third order energy leads off as R^{-9} rather than R^{-11} as for the 1SnS states and secondly it is found that if an attempt is made to evaluate B_{10} then the theory when carried to this length gives interference between the various terms and the resulting equations are not all decoupled.

equation of the type (17).

$$(h_c^o(c1) - \varepsilon_{ls_c}^o)\, \phi_{ls_c}^o(c1) = 0 \qquad (17)$$

where

$$h_c^o(c1) = -\tfrac{1}{2} \nabla_{c1}^2 - Z/r_{c1} + J_{ls_c}(c1) \qquad (18)$$

with

$$J_{ls_c}(c1) = \int \phi_{ls_c}^o(c2)\, (\,|r_{c1} - r_{c2}|\,)^{-1}\, \phi_{ls_c}^o(c2)\, d\tau_{c2} \qquad (19)$$

Substitution in the first order perturbation equation (6) of the relevant quantities clearly furnishes four equivalent equations of which (20) is representative:

$$(h_a^o(a1) + h_b^o(b2) - \varepsilon_{ls_a}^o - \varepsilon_{ls_b}^o)\, \psi'(a1, b2)$$

$$= - \Sigma H'_{ij}\, \phi_{ls_a}^o(a1)\, \phi_{ls_b}^o(b2) \qquad (20)$$

Expansion of ψ' as in (8) again yields a set of decoupled partial differential equations the solutions of which determine the B_n as in (22). (The factor four comes this time not from the normalisation of the zeroth function but from the need to account for the four equivalent equations (20). N.B. also the different sign convention for the B_n).

$$\left(-\tfrac{1}{2}\left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^2 \frac{\partial}{\partial r_{a1}}\right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^2 \frac{\partial}{\partial r_{b2}}\right)\right) + \tfrac{1}{2} \ell_i(\ell_i + 1)\, r_{a1}^{-2} \right.$$

$$+ \tfrac{1}{2} \ell_j(\ell_j + 1)\, r_{b2}^{-2} - Z/r_{a1} - Z/r_{b2} + J_{1s_a}(r_{a1}) + J_{1s_b}(r_{b2})$$

$$\left. - \varepsilon^{o}_{1s_a} - \varepsilon^{o}_{1s_b} \right) U_{ij}(r_{a1}, r_{b2})$$

$$= - M_{ij}\, r_{a1}^{i}\, r_{b2}^{j}\, R_{1s_a}(r_{a1})\, R_{1s_b}(r_{b2}) \qquad (21)$$

$$B_n = - 4.0\, M_{ij} \int U_{ij}(r_{a1}, r_{b2})\, r_{a1}^{i+2}\, r_{b2}^{j+2}$$

$$\times R_{1s_a}(r_{a1})\, R_{1s_b}(r_{b2})\, dr_{a1}\, dr_{b2} \qquad (22)$$

In a similar manner for the interaction of a two-electron system and a hydrogen atom using the uncoupled method the appropriate equation is (23) with the dispersion coefficients being evaluated from (24).

$$\left(-\tfrac{1}{2}\left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^2 \frac{\partial}{\partial r_{a1}}\right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^2 \frac{\partial}{\partial r_{b2}}\right)\right) + \tfrac{1}{2} \ell_i(\ell_i + 1)\, r_{a1}^{-2} \right.$$

$$+ \tfrac{1}{2} \ell_j(\ell_j + 1)\, r_{b2}^{-2} - Z/r_{a1} + J_{1s_a}(r_{a1}) - r_{b2}^{-1} - \varepsilon^{o}_{1s_a}$$

$$\left. + 0.5 \right) U_{ij}(r_{a1}, r_{b2}) = - 2.0\, M_{ij}\, r_{a1}^{i}\, r_{b2}^{j}\, R_{1s_a}(r_{a1})\, \exp(-r_{b2}) \qquad (23)$$

$$B_n = - 4.0\, M_{ij} \int U_{ij}(r_{a1}, r_{b2})\, r_{a1}^{i+2}\, r_{b2}^{j+2}$$

$$\times R_{1s_a}(r_{a1})\, \exp(-r_{b2})\, dr_{a1}\, dr_{b2} \qquad (24)$$

Obviously (21) and (23) differ very little from the equation (9) clearly exemplifying one of the great merits of the present approach (and indeed of the finite-difference techniques used throughout this work) viz. the ease by which the method can be applied to many problems without having to engage in extensive rederivation of theory or conver--sion of programs. For the actual calculations it was found that a range of grids containing 20(5)40 strips in each dimension gave almost seven figure accuracy on application of the Richardson process. The results will now be described:

B Results

Calculations were performed for a wide variety of systems M — M' or M — H where M, M' are two-electron atoms or ions, M being in some cases identical with M'. The zeroth functions employed were the same as those used in previous Chapters for various purposes viz. the basis sets of Clementi (C7) with the exception of H^- for which the corrected orbital of Curl and Coulson (C11) was utilised.

In Table 6.4 results* for three homonuclear systems are related together with previous uncoupled Hartree computations and the refined results of Davison (D10) which are based on a correlated wave--function and which are believed to be close to the exact values of the dispersion coefficients. Similarly Table 6.5 contains the values of the B_n for two mixed systems He — Li^+ and H^-—He. Before proceeding further it must be remarked that for the interaction of two charged

* These results are given to the maximum of five figures justified by the quality of the zeroth functions.

Table 6.4 Results for the dispersion coefficients for the $H^- — H^-$, He — He and $Li^+ — Li^+$ systems calculated within the uncoupled Hartree approach. Also included are the refined results of Davison based on a correlated wavefunction.

	This work	Other	
$H^- — H^-$			
Dipole–dipole term	1047.5	857.[a]	
Dipole–quadrupole term	1.3175×10^5		
Quadrupole–quadrupole term	7.7421×10^6		
Dipole–octupole term	2.0006×10^7		
He — He			
Dipole–dipole term	1.6641	1.6640[b]	1.47[c]
Dipole–quadrupole term	14.648	14.647	14.2
Quadrupole–quadrupole term	60.835	60.833	
Dipole–octupole term	121.35	121.34	
$Li^+ — Li^+$			
Dipole–dipole term	0.086905	0.086906[b]	
Dipole–quadrupole term	0.27008	0.27009	
Quadrupole–quadrupole term	0.39754	0.39755	
Dipole–octupole term	0.77799	0.77800	

[a,b] Uncoupled Hartree calculations of Deal and Kestner (D12) and of Singh (S21) respectively.

[c] Correlated wavefunction calculations of Davison (D10).

Table 6.5 Results for the dispersion coefficients for the He — Li^+ and H^-— He systems in the uncoupled Hartree approach. Also included are the refined results of Davison based on a correlated wavefunction.

	This work	Other	
He — Li^+			
Dipole–dipole term	0.34009	0.34009[a]	0.3023[b]
Dipole (He) - quadrupole (Li^+) term	0.50129	—	0.4745
Quadrupole (He) - dipole (Li^+) term	1.5706	—	1.5178
Total dipole–quadrupole term	2.0719	2.0719	1.9923
Quadrupole–quadrupole term	4.3657	4.3656	
Dipole (He) - octupole (Li^+) term	1.4126	—	
Octupole (He) - dipole (Li^+) term	13.276	—	
Total dipole–octupole term	14.688	14.688	
H^-— He			
Dipole–dipole term	25.243		26.5[b]
Dipole (H^-) - quadrupole (He) term	102.50		119.
Quadrupole (H^-) - dipole (He) term	1530.3		2026.
Total dipole–quadrupole term	1632.8		2145.
Quadrupole–quadrupole term	11571.		
Dipole (H^-) - octupole (He) term	821.67		
Octupole (H^-) - dipole (He) term	2.2327×10^5		
Total dipole–octupole term	2.2410×10^5		

[a] Uncoupled Hartree calculation of Singh (S21).

[b] Correlated results of Davison (D10).

species or of an ion with an uncharged ion the leading terms of the energy expansion $\Sigma B_n R^{-n}$ are due to sources other than the dispersive forces investigated here e.g. from charge-induced multipolar interactions. These also give the dominant contribution to the energy at reasonable internuclear distances, a good example being afforded by He — Li^+ for which it is found, using the results of this Chapter plus the polaris--abilities computed in Chapter 5, that only about ½% of the energy through R^{-6} arises from the dipole-dipole London coefficient. Despite this, as discussed by Davison (D10), the R^{-6} and higher dispersion terms may be of considerable importance for certain applications even where charged species are concerned.

From the Tables it may be observed that the present work is in harmony with the results of other workers who have used the uncoupled approach. Particularly noticeable is the quite excellent agreement with Singh (S21) who utilised the same zeroth functions as here but with a radically different method of calculation. It can also be seen that, as for the calculation of static polarisabilities, the Hartree method furnishes B_n which are somewhat too large in magnitude owing to the neglect of intraatomic correlation. This rule does not appear however to apply to the systems involving the hydride ion for which, as was noticed in 5, the excessively compact charge cloud given by the SCF function yields poor values for properties which are strongly dependent on this factor.

Finally in Table 6.6 results are listed for the interaction of He and Li^+ with H. For this case it can be noted, not surprisingly, that the error in the uncoupled Hartree values of the dispersion coefficients is about half that in the M - M' systems, the respective values being about 6 and 12% for the dipole-dipole terms.

Table 6.6 Results for the dispersion coefficients for the He - H and Li^+ - H systems in the uncoupled Hartree approach. Also included are the refined results of Davison.

	This work	Other	
He - H			
Dipole–dipole term	3.0219	3.02[a]	2.8173[b]
Dipole (H) - quadrupole (He) term	12.763		13.142
Quadrupole (H) - dipole (He) term	30.681		28.640
Total dipole–quadrupole term	43.444_8		41.782
Quadrupole–quadrupole term	245.18		
Dipole (H) - octupole (He) term	103.94_9		
Octupole (H) - dipole (He) term	544.86		
Total dipole–octupole term	648.81		
Li^+ - H			
Dipole–dipole term	0.52149		0.4907[b]
Dipole (H) - quadrupole (Li^+) term	0.74424		0.7470
Quadrupole (H) - dipole (Li^+) term	5.5826		5.2569
Total dipole–quadrupole term	6.3269		6.0039
Quadrupole–quadrupole term	15.010		
Dipole (H) - octupole (Li^+) term	2.0700		
Octupole (H) - dipole (Li^+) term	101.67		
Total dipole–octupole term	103.74		

[a] Uncoupled Hartree calculation of Dalgarno and Victor (D6).

[b] Correlated result of Davison (D10).

6.5 Conclusions

In this Chapter it has been seen that finite-difference methods can be employed to determine Van der Waals coefficients to great accuracy in an efficient manner within a given level of theory. For the interaction of two hydrogen atoms no approximations were required and the computed B_n may be regarded as exact to the precision given. However for the other problem which was studied the neglect of intra-atomic correlation is a serious source of error and to advance further with the calculation of dispersion forces for this type of system it will be necessary to account for this in some manner. At present this subject is under examination.

It is likely though that the techniques described here will be most useful in conjunction with semi-empirical methods for the solution of such problems as the evaluation of long-range interactions between alkali metal atoms. The reasons for this, with full supporting calculations, will be presented in Chapter 8.

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Chapter 7 A Finite-Difference Approach to the Calculation of Atomic Polarisabilities: Semi-Empirical methods.

7.1 Introduction

In Chapter 5 non-empirical approaches to the evaluation of atomic polarisabilities were considered. From that work however it would be apparent to the reader that such methods are at present only appropr--iate for calculations on small and medium sized atoms thus excluding from theoretical treatment most of the Periodic Table. Hence it is necessary to contemplate the use of semi-empirical techniques if an attempt is to made to calculate polarisabilities in generalised atomic systems, the justification for such an approach being twofold: it may yield information on systems which are inaccessible in the foreseeable future to accurate non-empirical treatment ; the results from semi-empirical methods may assist in the construction of non-empirical schemes for atoms which are now just at the limit of application of such techniques. The first of these is self-evident but for the second the reader may care to reflect on the instructive example of the determina--tion of the electron affinity of Li discussed in Chapters 3 and 9.

The topic which has been chosen for examination in this Chapter is the calculation of the polarisabilities of atoms containing a single occupied s orbital in the valence shell outside a closed core e.g. Na, K, Mg^{+}. The method which is employed for the solution of the problem is a pseudo or model potential approach in which the contribution of the core electrons to the polarisability is assumed to be negligible and in which the effect of the core on the valence electron is simulated by a model (or pseudo) potential, the parameterisation of which is

generally such as to reproduce exactly some experimentally ~~some experim--entally~~ observed property of the unperturbed system e.g. the valence electron spectrum. The model potential approach has a long history going back at least to the work of Hellmann (H7) and Gombas (G3) in 1935 and more recently it has found exploitation in the area of solid state physics following the important paper by Phillips and Kleinman (P5). It is however within the last five years that it has been the subject of considerable interest as a means of evaluating a variety of atomic pro--perties such as dispersion forces (K16), scattering phenomena (B12), photoionisation cross-sections (M2), and it is in this vein that the work of the present Chapter follows.

Here an equation for the perturbed orbital will be derived using the effective field as represented by the model potential and its solution will be effected for a number of atoms and ions using the finite-difference techniques introduced in Chapter 5. The latter, owing to their simplicity and flexibility, allow the examination of a number of different pseudopotential methods thus rendering possible an assessment of each of these and also eliminating to some extent the danger that the results obtained are merely an artifact of the particular form of poten--tial selected. In this manner it will be shown that for systems consist--ent with the primary assumptions of this Chapter, e.g. the alkali metals, accurate static and dynamic polarisabilities can be calculated which are in harmony with existing experimental and theoretical data.

7.2 Derivation of the model potential equation

In the problem under study, that of determining the polaris--ability of atomic systems containing but a single s valence electron, a

main assumption is that this quantity is essentially determined by the valence shell and hence core contributions can be neglected. For a core consisting entirely of closed shells this is physically reasonable being in addition supported by the work of Sternheimer (S25, S26) on the alkali metals and indeed by the examination of the SCPHF scheme in Chapter 5. The second major premise is that the effect of the core, including orthogonality constraints, can be represented accurately by a model potential. The validity of such an approach has been discussed extens--ively for several applications in the review by Weeks, Hazi and Rice (W5) but however its use in the present case will perhaps become more apparent from the derivation below:-

Since solely the contribution of the valence electron to the polarisability is of interest for the systems under investigation only the perturbation of the valence orbital is considered. Φ_v satis--fies the single-particle equation (1) with however the constraint (2) that it is orthogonal to the core orbitals.

$$(h^o(1) - \varepsilon_v^o)\,\Phi_v = 0 \qquad (1)$$

$$\int \Phi_v(1)\,\Phi_c(1)\,d\tau_1 = 0 \qquad (2)$$

for all core orbitals Φ_c.

Now following Weeks and Rice (W4) the non-orthogonal pseudowavefunction ψ_v^o yields the orthogonal valence orbital as in (3) by the application of the operator (1 - P) where P is the projection operator (4), projecting from any function that part of it lying within

the space of the core orbitals.

$$\Phi_v = (1 - P)\, \psi_v^o \tag{3}$$

where

$$P = \sum_c |\Phi_c\rangle\langle \Phi_c| \tag{4}$$

In this manner it is possible to rewrite (1) as (5).

$$(1 - P)\, (h^o(1) - \varepsilon_v^o)\, (1 - P)\, \psi_v^o = 0 \tag{5}$$

As shown by Phillips and Kleiman (P5) the equation for the pseudowavefun-
-ction can also be stated as (6), the term V^{PK} being a non-local repulsive potential which operates on an arbitrary function as in (7).

$$(h^o(1) + V^{PK}(1) - \varepsilon_v^o)\, \psi_v^o = 0 \tag{6}$$

$$V^{PK}(1)\, \xi = \sum_c (\varepsilon_v^o - h^o(1)) \langle \Phi_c | \xi \rangle \Phi_c \tag{7}$$

Thus far, although (6) gives an interesting insight into the effect of constraining the valence orbital to be orthogonal to the core functions, no simplification has been effected with the equations (5) or (6) being just as difficult to solve as (1). Neither has anything been said about the form of h^o. However in general it can be seen that $h_{PK}^o = h^o + V^{PK}$ consists of three terms in addition of course to the

Laplacian viz. (1) the nuclear attraction term $-Z/r$; (2) a term for the core/valence electron-electron repulsion ; (3) V^{PK} which is repulsive and which can be seen to be dependent on the azimuthal quantum number of ψ_v^o i.e. it is considerably different for s,p ..... orbitals.

Unfortunately the Phillips-Kleinman potential has one or two undesirable features for the purposes of this Chapter, the principal being that it is <u>not</u> unique and admits of an arbitrary core contribution to the pseudowavefunction even although variational collapse is prevented (W5). It is hence convenient to introduce a model Hamiltonian h_m^o which attempts to allow for the effects listed in the previous paragraph by a local potential V_m which is chosen in some manner as will be described in the next section, a major property being though that it is repulsive in the core region if the valence orbital has precursors in the core. Such a simplification may appear very drastic but it is not entirely unreasonable for systems for which there is not a substantial penetration of the core by the valence orbital provided that V_m is asymptotically correct. Thus for cases such as the alkali metal atoms for which there is a credible separation of the core and valence shell the above assumptions are probably quite proper as will be seen. An important point though is that it is felt necessary to introduce an ℓ dependence into the model potential since V^{PK} is in turn strongly dependent on this factor e.g. for Li $1s^2 2p$ V^{PK} acting on the 2p orbital is zero since the core does not contain any orbitals of p symmetry but for the 2s orbital for the configuration $1s^2 2s$ this is clearly not so. Hence all the model potentials examined here have the general form (8).

$$V_m = \sum_\ell |\ell\rangle V_\ell(r) \langle\ell| = \sum_\ell V_\ell(r)\ \Omega_\ell \qquad (8)$$

In (8) Ω_ℓ is a projection operator over the subspace of spherical harmonics of a given ℓ.

Now if the system is perturbed by the multipolar operator (9) then on application of perturbation theory the equation (10) for the perturbed orbital is obtained.

$$h^1(1) = r_1^\ell P_\ell(\cos\Theta_1) \tag{9}$$

$$\left(-\tfrac{1}{2}\nabla_1^2 + \sum_\ell |\ell\rangle V_\ell(r_1)\langle\ell| - \varepsilon_v^o \right) \psi_v^1 = \left(\varepsilon^1 - h^1(1) \right) \psi_v^o \tag{10}$$

On reduction of (10) to radial form (11) is obtained, the most noticeable feature of which is that the model potential operating on the perturbed function is that apposite to a valence function of ℓ symmetry rather than that for the unperturbed s state.

$$\left(-\tfrac{1}{2}\frac{d^2}{dr_1^2} + \tfrac{1}{2}\ell(\ell+1) r_1^{-2} + V_\ell(r_1) - \varepsilon_v^o \right) f_\ell(r_1) = -r_1^\ell P_v^o(r_1) \tag{11}$$

where P_v^o is the radial distribution function for the zeroth orbital.

A similar analysis can also be applied for the frequency-dependent problem giving the local, uncoupled equations (12) for the functions f^+ and f^-.

$$\left(-\tfrac{1}{2}\frac{d^2}{dr_1^2} + \tfrac{1}{2}\ell(\ell+1)\, r_1^{-2} + V_\ell(r_1) - \varepsilon_v^o \pm \omega \right) f_\ell^{\pm}(r_1)$$

$$= -r_1^{\ell} P_v^o(r_1) \qquad (12)$$

The equations (11) and (12) can clearly be very easily solved using the finite-difference methods examined in preceding Chapters, the versatility of this type of approach making it possible to investigate the use of several different model potentials. These will now be described.

7.3 Choice of model potential and methods of solution

In this work four different types of model potential were examined. These potentials, here designated as Types A, B, C and D, will now be described in turn:

A Type A: Hellmann potential

The first form of potential selected for investigation was an ℓ-dependent version of the Hellmann potential as given by equation (13).

$$V_\ell(r) = A_\ell\, r^{-1} \exp(-2\kappa_\ell r) - Z/r \qquad (13)$$

where A_ℓ and κ_ℓ are parameters to be determined and Z is the excess charge on the core i.e. Z=1 for Na, Z=2 for Mg^+ and so on.

As far as the choice of parameters is concerned these were chosen such that the first eigenenergy corresponding to each V_ℓ was set

equal to the negative of the ionisation potential of the first ℓ state of the atom. Now it is evident that for each V_ℓ two parameters A_ℓ and κ_ℓ have to be determined and accordingly there is some arbitrariness in these if, as above, only one piece of experimental data or other constraining factor is incorporated for each V_ℓ. However it is felt that great precision is not required in the form of the potential provided it has certain properties viz.

1/ The correct Coulombic asymptotic behaviour is reproduced.

2/ For systems for which the valence orbital(s) has precursors in the core the potential must be repulsive in this region.

3/ The spectrum for the valence electron is fairly well simulated.

In support of the above view it was found by the author that if 'reason--able' values are chosen for the A factors and the κ parameters fixed accordingly then the results for polarisabilities and other such proper--ties were relatively invariant.* This is of course very desirable since if the calculated quantities were strongly dependent on the choice of parameters it would be difficult to consider the present approach to be at all reliable. Overall it may be remarked that the above is in accord with the ideas of Weeks, Hazi and Rice (W5) who consider that the model potential is a good approximation to the true potential outside the core but should be viewed as only a fictitious potential inside the latter. Hence for properties such as polarisabilities which are highly dependent on the outer parts of the valence wavefunctions (cf. Chapter 5) satisfactory values of these quantities may be expected if the outer regions of the zeroth function and the effective potential can be

* Similar observations have been made by other authors e.g. Schwartz and Switalski (S12) for other applications of the model potential method.

reproduced correctly.

For the parameterisation process A_ℓ based on those listed by Schwartz (S13) were taken. κ_ℓ values were determined by solving the eigenvalue equation (14) in the manner of Chapter 4 for a range of κ, interpolating the latter to obtain an exponent κ' which approximately reproduces the relevant orbital energy and then repeating the procedure over a narrower band of κ about κ' until the potential gave an ε_v^o which differed from the experimental energy only by a prescribed tolerance (generally 0.001 eV here).

$$\left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \tfrac{1}{2}\ell(\ell+1)\, r^{-2} + V_\ell(r) - \varepsilon_v^o \right) f_\ell(r) = 0 \qquad (14)$$

Selections of parameters so determined are collected in Table 7.1 for a variety of systems, it being found that the κ_ℓ with a very few exceptions do not differ greatly from those given for some atoms by Schwartz (S13), the latter's potentials yielding a typical overshoot of 0.01 eV or less in the ε_v^o when these are determined numerically in the manner of this work. This may be contrasted with the spectrum found when the Hellmann potentials of Szasz and McGinn (S30) are used and (14) is again solved accurately. In Table 7.2 the energies of the ns states of Sr^+ are listed for this parameterisation* and it is obvious that the computed energies vastly overshoot the experimental values even for the ground state, the reason for this being Szasz and McGinn's assumption

* Similar results are obtained for many other systems ..... those in Table 7.2 are in no way exceptional.

Table 7.1 A selection of parameters for the Type A (Hellmann) potential as determined in the text. Atomic units are used as throughout this work.

System	A_s	A_p	κ_s	κ_p
Li	10.0	-2.0	1.0997	1.1718
Na	14.0	14.0	1.1324	1.1128
K	18.0	18.0	0.93193	0.81609
Rb	26.0	26.0	0.96897	0.78268
Cs	34.0	34.0	0.93048	0.73015
Be^+	20.0	-3.0	1.6797	1.9993
Mg^+	30.0	30.0	1.4259	1.4454
Ca^+	50.0	50.0	1.1670	1.0592
Sr^+	60.0	60.0	1.1017	0.94329
Ba^+	70.0	70.0	0.99985	0.83862
Ra^+	80.0	80.0	1.0488	0.83308
Cu	30.0	-5.0	3.0598	1.2524
Zn^+	60.0	60.0	2.2497	2.4425

Table 7.2 A comparison of the s states valence electron spectrum of Sr^+ computed using a Hellmann type of pseudopotential with the parameterisation of Szasz and McGinn (S30) with the experimentally observed spectrum.

	Computed energy[a]	Experimental energy
5s	-11.995	-11.027
6s	-5.948	-5.110
7s	-3.413	-2.975
8s	-2.194	-1.949
9s	-1.525	-1.377
10s	-1.120	-1.024
11s	-0.857	-0.792
12s	-0.677	-0.630

[a] All energies are in eV.

that the pseudowavefunction for the lowest pseudostate can be represented by a hydrogenic function. Clearly this leads to very substantial errors as has been previously pointed out by Simons and Nazziotti (S18) amongst others and illustrates the need to perform the parameterisation accurately by either numerical methods or by an exhaustive variational procedure.

For the polarisability calculations a similar approach to that employed in Chapter 5 was used with the appropriate potential inserted in equation (11). No difficulties were experienced in the com-putations, the Richardson process yielding satisfactory extrapolation tables. A word is however apposite about the choice of the zeroth function which was taken to be the solution of equation (14) for the lowest orbital s state. While the form of the pseudowavefunction is almost certainly correct outside the core there is however, as discussed by Bardsley (B2), some uncertainty over the normalisation of the function. Here though each pseudowavefunction was normalised to 1, it being possible to see on reflection that owing to the repulsive form of s model potentials in the core region errors due to this source are negligible in comparison to those from other factors.* In addition to admit of any other possiblity greatly increases the complexity of the problem as it becomes necessary to define the core functions in some manner. In conclusion it seems probable that if the assumption about the normalisation is incorrect then it will be because there is not a reasonable core/valence orbital separation which would in any case render the whole model potential

* Cf. also comparison of Hellmann pseudowavefunctions and SCF functions in Schwartz (S13).

approach invalid for the system. This point will be returned to in section 7.4.

B Type B: 'Cutoff' potential

The second choice of model potential was a version of the 'cutoff' potential employed by many workers for various types of pseudo--potential calculation.*

This potential is defined as in equations (15) and (16) where (15) applies for $r \leqslant R_c$ and (16) other than for this range, R_c being a 'core' radius to be fixed.

$$V_\ell(r) = -B_\ell \qquad (15)$$

$$V_\ell(r) = -Z/r \qquad (16)$$

For the s states B_s is set equal to |ground state ionisation potential| and R_c is determined such that the modulus of the eigenvalue from equation (14) is also equal to this quantity. For p and higher states R_c is kept constant but B_ℓ is varied so as to yield the correct lowest ℓ state energy as before. The justification for the form of the potential has been extensively dealt with by Weeks and Rice (W4) and Weeks, Hazi and Rice (W5) and it is sufficient to note that again the model potential

* See for example Weeks, Hazi and Rice (W5) and references contained therein.

has the correct asymptotic behaviour while in the core region it is only weakly attractive or is repulsive.

For the parameterisation a similar iterative scheme to that employed for the Hellmann potential was utilised and a list of these quantities for a few systems is given in Table 7.3.. Analogous proced--ures to that for the Type A potential were also used for the evaluation of the polarisabilities there being only one uncertainty over the results. This is due to the discontinuity in the cutoff potential which makes the application of the Richardson extrapolation process less certain than for the smooth potentials generally dealt with before (cf. though Chapter 4). However although greater numbers of grid points are required to give accuracy the computed values of the various quantities appear reliable to the precision given as different sets of grids yield identical extra--polants. Also for systems examined by Weeks and Rice (W4) the parameters obtained variationally by them are in harmony with those found numerically in this work.

C Type C: Modified Coulomb approximation

For this particular scheme a rather different application of the model potential approach is made. Here the zeroth wavefunction is taken to be the asymptotically correct Coulomb wavefunction (17) as given by Bates and Damgaard (B5).

$$\psi_v^o(r) = N\, r^{-l}\, W_{n^*,\, l+\frac{1}{2}}(2Zr/n^*) \qquad (17)$$

Table 7.3 A selection of parameters for the Type B model potential as determined in the text. All quantities are in atomic units.

System	R_c	B_s	B_p
Li	1.9800	0.19810	0.76252
Na	2.1408	0.18886	0.26129
K	2.7871	0.15952	0.085228
Rb	2.9485	0.15350	-0.034575
Cs	3.2702	0.14311	-0.078876
Be^+	1.2977	0.66925	2.2827
Mg^+	1.7246	0.55239	0.75449
Ca^+	2.4003	0.43628	0.34257
Sr^+	2.6468	0.40533	0.15552
Ba^+	3.0082	0.36752	0.077578
Ra^+	2.9594	0.37266	-0.015474
Cu	1.0160	0.28386	3.0621
Zn^+	1.3215	0.66006	1.2218

where $\ell = 0$ and

$$W_{n^*,\,\ell+\frac{1}{2}}(2Z2/n^*) = \exp(-Zr/n^*)\,(2rZ/n^*)^{n^*}\,(1 + \sum_{t=1}^{\infty} \frac{a^t}{r^t}) \qquad (18)$$

with

$$a_1 = \tfrac{1}{2}\, n^*\, Z^{-1}\,(\ell(\ell+1) - n^*(n^*-1)) \qquad (19)$$

and

$$a_t = a_{t-1}\,(\tfrac{1}{2}\, n^*\, Z^{-1}\,(\ell(\ell+1) - (n^*-t)(n^*-t+1))) \qquad (20)$$

As before Z is the excess charge on the core and the effective quantum number is defined as in (21)

$$\varepsilon_v^o = -\tfrac{1}{2}\, Z^2\, (n^*)^{-2} \qquad (21)$$

Again following Bates and Damgaard (B5) the normalisation factor is chosen as (22).

$$N = ((n^*)^2\, \Gamma(n^* + \ell + 1)\, \Gamma(n^* - \ell)/Z)^{-\frac{1}{2}} \qquad (22)$$

Adelman and Szabo (A4, A5), who give a critique of a previous attempt by Dalgarno and Pengelly (D4) to apply the Coulomb approximation to the calculation of atomic polarisabilities, have demonstrated that the use of a simple Coulombic Hamiltonian for H^o is inadequate and that it is necessary to introduce a pseudopotential as in 7.2. These authors, who

employ the Schwartz-Tiemann (S9) transform technique to obtain the perturbed functions, select a model Hamiltonian of the type (23) as this is convenient for the application of their analytic method of solution.

$$H^{o} = -\tfrac{1}{2}\nabla^{2} - Z/r + \tfrac{1}{2}(\lambda(\lambda+1) - \ell(\ell+1))\, r^{-2} \qquad (23)$$

where λ is again such that the lowest eigenvalue of ℓ-type symmetry agrees exactly with the experimental datum.

It should be emphasised that any of the other model potentials discussed in this Chapter could be used instead of that in (23), this merely being an expedient choice of Adelman and Szabo. Here though it is retained so that a check could be made on the approximations employed both by Adelman and Szabo and by the author in their different approaches to the solution of (11).

For the determination of the polarisabilities from the equation (11) the infinite series (17) for the Coulomb wavefunction has to be approximated in some manner. In this work the apparently very severe restriction of truncating the expression for the Whittaker function such that only positive powers of r are included was made. Superficially this is a very drastic assumption but however it is in the spirit of the work on oscillator strengths by Bates and Damgaard (B5). It is also fairly easy to see that after the first two or three terms only near the nucleus will the zeroth wavefunction be materially affected whereas it is the outer parts of this function which determine the a_{ℓ}. This question will be returned to in the discussion.

Finally the parameters for the pseudopotential can conveniently be obtained from the compilations of Simons (S16, S17) with though

corrections being needed in one or two cases owing to misprints.

D Type D: G1 Atomic Effective Potential

The final type of model potential is the G1 Atomic Effective Potential due to Kahn and Goddard (K1). This is an ab initio effective potential derived from a Spin Optimised Hartree-Fock calculation (S2). However in this formalism, in contrast to the normal Hartree-Fock proc-edure, the orbitals are not constrained to be orthogonal and are generally nodeless (cf. the pseudowavefunctions of this Chapter). In addition the single-particle potentials acting on the valence orbitals are found, again in analogy to model potential theory, to be repulsive in the core region. Thus it is reasonable to attempt to use these poten-tials, once determined from a relatively elaborate calculation, in the manner one may employ more conventional pseudopotentials and indeed several successful such applications have been reported.*

For the present studies valence orbitals and p-type potentials were regenerated for Li — F^{6+} from the data of Kahn and Goddard (K1) using the Sternheimer approach suggested by these authors.

Finally before a discussion of the results for the polarisa-bilities one may note the fairly good representation of the one-electron spectrum by the different pseudopotentials. In Table 7.4 results are given for the s and p states of Li and it can be observed that these are generally in harmony with the experimental values especially, as would

* See Kahn and Goddard (K1) and previous references contained therein.

Table 7.4 A comparison of values for the energies of the s,p states of Li employing the various pseudopotential approaches described in the text. Energies are in eV.

	Type A[a]	Type B	Type C[b]	Type D[c]	Experimental[d]
2s	-5.390	-5.390	-5.390	-5.338	-5.390
3s	-2.028	-2.038	-2.030	-2.035	-2.018
4s	-1.055	-1.060	-1.056	-1.060	-1.050
5s	-0.646	-0.648	-0.646	-0.648	-0.643
6s	-0.435	-0.437	-0.436	-0.437	-0.434
7s	-0.313	-0.314	-0.313	-0.309	-0.312
2p	-3.543	-3.543	-3.543	-3.504	-3.543
3p	-1.558	-1.553	-1.553	-1.547	-1.557
4p	-0.870	-0.868	-0.868	-0.866	-0.870
5p	-0.555	-0.553	-0.553	-0.552	-0.554
6p	-0.384	-0.383	-0.383	-0.382	-0.384
7p	-0.281	-0.281	-0.281	-0.267	-0.281

[a] Type of pseudopotential employed. See text for details.

[b] See text for full explanation of the use of this potential.

[c] Taken from Kahn and Goddard, reference (K1).

[d] Taken from Moore, reference (M7). Values for p states are weighted average of spin-orbit levels.

Table 7.5 A comparison of values for the energies of the d,f states of Li employing the various pseudopotential approaches described in the text. Energies are in eV.

	Type A[a]	Type B	Type C[b]	Type D[c]	Experimental[d]
3d	-1.512	-1.514	-1.513	-1.512	-1.513
4d	-0.851	-0.852	-0.851	-0.851	-0.851
5d	-0.544	-0.545	-0.544	-0.544	-0.544
6d	-0.378	-0.378	-0.378	-0.378	-0.378
7d	-0.278	-0.278	-0.278	-0.266	-0.278
4f	-0.850	-0.850	-0.850	—	-0.850
5f	-0.544	-0.544	-0.544	—	-0.543
6f	-0.378	-0.378	-0.378	—	—
7f	-0.278	-0.278	-0.278	—	—

[a] Type of pseudopotential employed. See text for details.

[b] See text for full explanation of the use of this type of potential.

[c] Taken from Kahn and Goddard, reference (K1).

[d] Taken from Moore, reference (M7).

be expected, as n increases.* Similarly in Table 7.5 results are given for the d and f states using the p-type potentials (with the exception of Type C for which the d potential is easily found), the good agreement obtained illustrating the well-known fact that, to a good approximation, the same potential can be used for all states which do not have precursors in the core.

7.4 Results and discussion

In Table 7.6 the dipole polarisabilities of the alkali metal atoms computed using the various pseudopotential methods are listed together with other theoretical and experimental estimates of these quantities. Similarly in Table 7.7 quadrupole polarisabilities are given, the Type C approach only being employed in this case although full values for Li for all potentials are displayed in Table 7.10.

It is immediately noticeable that for the dipole polarisabilities of the alkali metals the choice of pseudopotential method is relatively immaterial with in the worst case the spread about the median value being less than $\pm$ 2%. Even a radical change of parameterisation appears to have comparatively little effect on the polarisability. For example using the Hellmann potential A factors of Szasz and McGinn (S30) and suitable exponents to correctly reproduce the ground and first excited p state energies yields 149.8 a.u. for the dipole polarisability of Na (cf. Sternheimer (S25) value). All of the results with the possible

* The anomalous results for the 7s and 7p states using the Type D potential are probably a consequence of the inadequate radial cutoff chosen by Kahn and Goddard (K1) for their finite-difference determination of the one-electron spectrum.

Table 7.6 A comparison of values of the dipole polarisability of the alkali metal atoms from the pseudopotential approaches in this Chapter and from the work of others.

	Li	Na	K	Rb	Cs
Pseudopotential A	164.3[a]	163.1	297.0	328.0	416.0
Pseudopotential B	163.7	160.9	290.0	318.1	400.9
Pseudopotential C	166.1	162.0	290.2	319.6	401.4
Pseudopotential D	166.1	—	—	—	—
Sternheimer (S25)	167.0	150.7	290.0	307.0	413.0
CPHF[b]	170.3	168.2	—	—	—
Other[c]	167.6	—	—	—	—
Experimental[d]	148 ± 13	165 ± 11	305 ± 22	329 ± 23	427 ± 31

[a] Fourth digit is not significant.

[b] Mukherjee, Moitra and Mukherji, reference (M8).

[c] Many-body perturbation theory result of Chang, Pu and Das (C2).

[d] Li value is that of Chamberlain and Zorn (C1), others are from Hall and Zorn (H1).

Table 7.7 A comparison of values of the quadrupole polarisabilities of the alkali metal atoms.

	This work[a]	Sternheimer[b]	CPHF[c]
Li	1405.	1446.	1517.
Na	1811.	1804.	2191.
K	4719.	5097.	—
Rb	6087.	6300.	—
Cs	1.026×10^4	1.062×10^4	—

[a] Using Type C pseudopotential. For the other potentials examined full results are given for Li in Table 7.10.

[b] Reference (S26).

[c] Reference (M8).

exception of those for Li appear to be in harmony with the experimentally observed estimates of the polarisabilities. The agreement with other calculations is also good, probably the two most refined being the CI study of Stacey and Dalgarno (S24) and the many-body perturbation theory computation of Chang, Pu and Das (C2), both for Li. These two groups of workers obtain a dipole polarisability for this system of 163.0 or 167.6 a.u. respectively which may be compared with the present values of 163.7 to 166.1 a.u..

It is perhaps worth commenting on the present application of the Coulomb approximation as opposed to the method of Adelman and Szabo (A4, A5). As was seen in the previous section for this work it was decided to make the superficially drastic approximation of truncating the radial distribution function for the Coulomb wavefunction so as to include only positive powers of r, the justification being that only such terms would contribute significantly to the polarisability as this property is highly dependent on the outer parts of the unperturbed orbital. This assumption appears to be vindicated by Table 7.8 in which dipole and quadrupole polarisabilities for a number of systems derived using the two different computational approaches are compared. Overall the differences are generally marginal and may in part be accounted for by minor changes in the parameterisation of the pseudopotentials. For two cases for which error bounds are given by Adelman and Szabo (A4) viz. ½ and 3% for the quadrupole polarisabilities of Rb and Cs respectively*

* Unfortunately these authors do not indicate the direction in which the error acts. Hence for α_q for Cs the error in the present value may be either negligible or up to 5½%.

Table 7.8 A comparison of the present results using a Coulomb-like approximation and those of Adelman and Szabo.

	a_d^a	a_d^b	a_q^a	a_q^b
Li	166.1	164.	1405.	1398.
Na	162.0	$160._6$	1811.	1803.
K	290.3	$291._5$	4719.	4700.
Rb	319.6	$325._3$	6087.	6102.
Cs	401.4	$411._7$	1.026×10^4	1.051×10^4
Be^+	25.11	24.8	53.22	53.0
B^{2+}	8.080	7.96	7.213	6.99
Mg^+	33.78	34.0	150.7	150.

[a] This work.

[b] Adelman and Szabo, references (A4, A5).

the differences in the two sets of polarisabilities are $\frac{1}{4}$ and $2\frac{1}{2}\%$ suggesting that the present mode of application of the Coulomb approxi-mation is satisfactorily accurate.

For the alkali metals one may reasonably anticipate fairly consistent results since, on physical grounds, these systems would appear to conform well to the various criteria delineated in sections 7.2 and 7.3 for the successful application of the type of semi-empirical methods used in this Chapter. However for other systems e.g. positive species this may not necessarily be the case and it is hence interesting to examine results for a wider range of atoms and ions. To this end dipole and quadrupole polarisabilities are listed in Tables 7.9 and 7.10 for the sequence Li — F^{6+}, all four model potential methods being employed as before.* Surprisingly the α_ℓ derived from the different potentials are remarkably consistent even for the more highly ionised species for which it might be thought that approximations such as the implicit assumption of a 'separation' of the core and valence shells would be poor. However some breakdown of these premises is apparent in the drift in the spread of the different sets of polarisabilities when one moves from the L.H.S. to the R.H.S. of the Row of the Periodic Table. Agree-ment with the other theoretical values which are included in the Tables is also good and although there is some indication from the refined studies of Stacey (S23) and Flannery and Stewart (F1) of an inaccuracy of a few per cent in the dipole polarisability of the most positive

* For potentials A, B and D the p-type potential was employed for the calculation of the quadrupole polarisabilities.

Table 7.9 A comparison of the dipole polarisabilities of the sequence Li — F^{6+}.

	Type A[a]	Type B	Type C	Type D	Other results		
Li	164.3	163.7	166.1	166.1	170.[b]	161.8[c]	169.[d]
Be^{+}	24.81	25.02	25.11	24.22	25.0	23.8	24.6
B^{2+}	8.029	8.032	8.080	7.735	7.96	7.63	7.83
C^{3+}	3.553	3.655	3.552	3.411	3.50	3.37	3.44
N^{4+}	1.877	1.893	1.865	1.798	1.84	1.78	1.80
O^{5+}	1.109	1.120	1.096	1.063	1.08	1.05	1.06
F^{6+}	0.7070	0.7152	0.6957	0.6798	0.688		0.678

[a] Type of model potential employed. See text for details.

[b] Lahiri and Mukherji (L1).

[c] CI calculation reference (S23).

[d] Accurate calculation based on open-shell wavefunction by Flannery and Stewart (F1).

Table 7.10 A comparison of values of the quadrupole polarisabilities of the sequence Li — F^{6+} employing the various pseudopotential approaches described in the text.

	Type A[a]	Type B	Type C	Type D	Other results		
Li	1403.	1394.	1405.	1443.	1517.[b]	1446.[c]	1494.[d]
Be^{+}	53.01	52.83	53.22	51.44	55.4		55.62
B^{2+}	7.012	6.917	7.213	6.599	7.23		7.235
C^{3+}	1.583	1.581	1.590	1.463			1.618
N^{4+}	0.4851	0.4800	0.4871	0.4429			0.4926
O^{5+}	0.1814	0.1796	0.1820	0.1642			0.1835
F^{6+}	0.07802	0.07729	0.07829	0.07022			

[a] Refers to pseudopotential employed. See text for explanation.

[b] Taken from CPHF calculation of Mukherjee, Moitra and Mukherji (M8).

[c] From work of Sternheimer (S26).

[d] Uncoupled Hartree-Fock calculations of Langhoff and Hurst (L3).

species it is difficult to give a definitive judgement on this question in the absence of further accurate information.

This type of failure of the naive model presented here is however more apparent for other positive ions, results for which are displayed in Table 7.11. Evidently, just as would be expected, there is a deterioration in the reliability of the calculations both as the charge on the ion increases and as one proceeds down the Periodic Table. Clearly the simulation of the effect of the core by a simple local potential becomes steadily less satisfactory but nevertheless the computed polarisabilities still give a useful indicator of the order of magnitude of these quantities particularly when one considers the difficulties involved in performing accurate calculations for the heavier species.

Finally in Tables 7.12 and 7.13 the frequency-dependent dipole polarisabilities of Li and Na are listed for a series of wavelengths up to the first resonance and in Figure 7.1 the Hellmann potential results are compared for these two systems. Again all of the potentials yield consistent results though there is some indication that those from the Type B potential are somewhat inaccurate near the resonance probably as a consequence of the unphysical discontinuity in the potential. Unfortunately there is a paucity of data in the literature with which to effect a suitable comparison but however both Stacey and Dalgarno (S24) and Moitra and Mukherjee* give a graph of the dynamic polarisability of

* See Moitra, R.K., and Mukherjee, P.K., Intern.J.Quantum Chem., 6, 211 (1972).

Table 7.11 A comparison of dipole polarisabilities of some positive ions derived using the various pseudopotential approaches.

	Type A[a]	Type B	Type C	Type D
Be^+	24.81	25.02	25.11	24.22
Mg^+	35.81	34.93	33.78	—
Ca^+	81.46	78.06	72.64	—
Sr^+	98.90	94.03	87.75	—
Ba^+	136.4	128.5	118.9	—
Al^{2+}	14.72	14.29	13.18	—
Si^{3+}	7.731	7.476	6.653	—
P^{4+}	4.628	4.463	3.845	—
S^{5+}	3.012	2.898	2.426	—
Cl^{6+}	2.075	1.996	1.626	—

[a] Type of pseudopotential employed. See text for details.

Table 7.12 Results for the frequency-dependent dipole polarisability of Li using the pseudopotential approaches described in the text. Polarisabilities are in a.u..

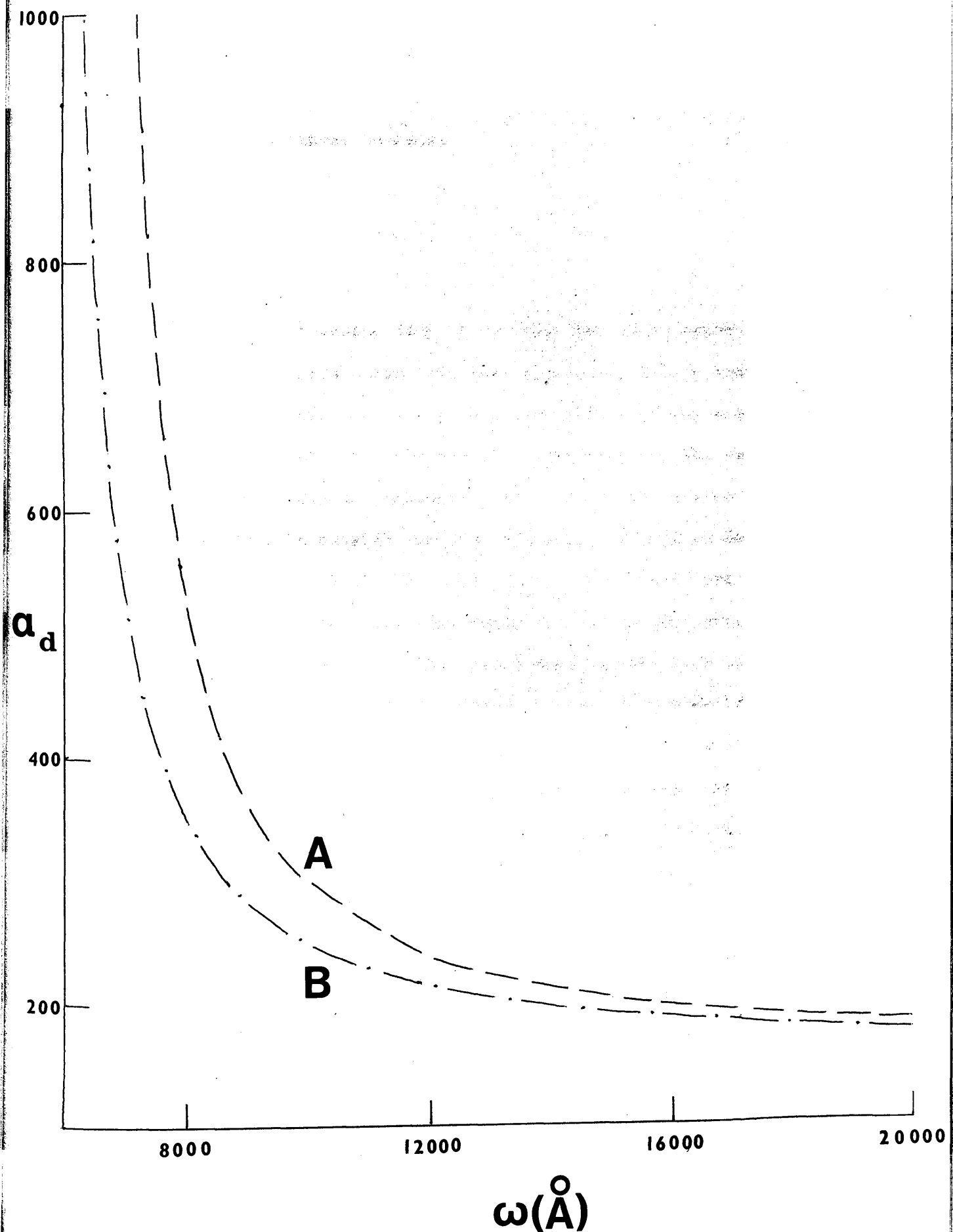
Wavelength (Å)	Type A	Type B	Type C	Type D
∞	164.3	163.7	166.1	166.1
50000.0	167.3	165.7	169.3	169.2
40000.0	169.0	167.4	171.0	170.9
30000.0	172.9	171.2	175.0	174.9
25000.0	176.9	175.2	179.1	179.1
20000.0	185.0	183.1	187.2	187.3
15000.0	205.0	202.9	207.6	208.1
10000.0	297.7	293.9	301.6	304.5
9750.0	310.8	306.8	315.0	318.3
9500.0	326.3	322.1	330.8	334.8
9250.0	345.1	340.4	349.8	354.6
9000.0	368.1	362.8	373.1	378.9
8750.0	396.8	390.8	402.2	409.4
8500.0	433.6	426.7	439.6	448.9
8250.0	482.5	474.3	489.3	501.7
8000.0	550.7	540.3	558.5	576.0
7750.0	651.7	637.8	661.2	687.9
7500.0	817.7	796.3	829.5	875.6
7250.0	1138.	1098.	1154.	1254.
7000.0	2012.	1870.	2043.	2411.
6900.0	3011.	2702.	3057.	4004.
6800.0	6249.	5059.	6351.	1.368×10^4

Table 7.13 Results for the frequency-dependent dipole polarisability of Na using the pseudopotential approaches described in the text. Polarisabilities are in a.u..

Wavelength (Å)	Type A	Type B	Type C
∞	163.1	160.9	162.0
50000.0	165.4	162.5	164.3
40000.0	166.7	163.8	165.6
30000.0	169.6	166.7	168.5
25000.0	172.7	169.7	171.5
20000.0	178.6	175.5	177.4
15000.0	192.8	189.5	191.5
10000.0	249.6	245.3	247.9
9750.0	256.6	252.3	255.0
9500.0	264.7	260.3	263.0
9250.0	274.1	269.5	272.3
9000.0	285.0	280.2	283.2
8750.0	298.0	293.0	296.1
8500.0	313.5	308.2	311.5
8250.0	332.3	326.8	330.3
8000.0	355.8	350.0	353.6
7750.0	385.8	379.5	383.4
7500.0	425.2	418.4	422.6
7250.0	479.4	471.8	476.5
7000.0	558.4	549.8	555.0
6800.0	653.2	643.5	649.3
6500.0	913.4	901.0	908.1
6250.0	1466.	1451.	1458.
6000.0	4629.	4646.	4603.

Figure 7.1

A comparison of the frequency-dependent polarisabilities of Li and Na (A and B respec--tively) as computed from the Hellmann type of model potential. Polarisabilities are in a.u. but the wavelength of the incident radiation is in Å.


1000
800
600
400
200
α_d
A
B
8000
12000
16000
20000
$\omega(\mathring{A})$

Li which appears to be in harmony with the model potential work though in the absence of a listing of the polarisability at prescribed frequencies proper assessment cannot be made.

7.5 Conclusions

It is of course easy to crticise the naive approach taken here:- the potentials chosen are very simple and fairly arbitrary in form and little regard has been paid to the effect of the core on the polarisability. Nonetheless the overall consistency of the results suggests that the original assumption that it is the portion of the valence wavefunction outside the core which is dominant in determining the polarisability is valid for atoms such as the alkali metals for which a separation into valence and core contributions is credible.

In this Chapter it has again been evident that the finite-difference approach to the determination of the first order functions has been advatageous in that it has enabled the use of several differ--ent potentials to be examined and thus minimise to some extent the poss--ibility that the calculated α_ℓ are merely an artifact of a specific form of potential. Accordingly their use may perhaps be commended for future work of this kind both in the extension of the model potential method to other types of system and to performing calculations with rather more refined potentials as for example are discussed by Bardsley (B2). However in the latter case care will have to be taken in the construction of more elaborate model potentials and one must beware of succumbing to the remarkably strong temptation to resort to the ad hoc addition of more and more parameters of little or no physical signifi--cance in order to obtain 'good' results.

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Chapter 8 A Finite-Difference Approach to Long-Range Interactions: Semi-Empirical Methods.

8.1 Introduction

In Chapter 6 a new computational approach to the calculation of long-range interactions between simple atomic systems was delineated. However, as was the case for the atoms whose polarisabilities were obt--ained in Chapter 7, such non-empirical investigations are not easily extended to the substantially heavier atoms which are generally of the most chemical and physical interest and thus, at the present time, semi-empirical methods must be employed. It is hence the purpose of this part of the work to so widen the scope of the finite-difference approach to long-range interactions beyond the narrow range of problems dealt with in 6, the particular topic chosen for examination being the evaluation of dispersion coefficients for pairs of atoms of the alkali metals.

It was seen in 7 that if a problem is sufficiently well-posed then semi-empirical methods will yield results which are not necessarily inferior to those from non-empirical calculations for even quite small atoms for which the latter can be accurately executed (e.g. cf. values of the polarisabilities of Li and Na). Here, both on physical considerations and from the encouraging results for polarisabilities found in the previous Chapter, it is believed that the subject of this investigation meet such a criterion if pseudopotential techniques are again employed in the computations. As for the preceding work it is felt that if the outer, near-Coulombic part of the atomic potentials can be correctly represented and also a realistic charge distribution given for the valence orbitals then the exact form of the model potential will

be relatively unimportant within reasonable limits.

The determination of Van der Waals coefficients for alkali metal atom pairs is of no little interest as there is a discrepancy between theoretical and experimental values of these quantities, the former being of the order of two or three times the magnitude of the latter. Various reasons have been advanced for this disparity* with probably the most popular being that the empirical data has been wrongly interpreted owing to the importance of terms other than B_6 in the region of the potential which is effective for the scattering experiments which are employed in the attempts to determine the London coefficients. In turn these other terms could be due either to the persistence of the type of forces dominant at short range to fairly large internuclear separa--tions or to higher dispersion coefficients being large (cf. the excited state interactions of H atoms discussed in Chapter 6). There is evidence that both these explanations are apposite:- Kutzelnigg and Gelus (K17) using a special MCSCF procedure and Bardsley (B2) employing a model potential formalism have found evidence of appreciable singlet-triplet branching up to about 15.0 a.u. for the Li-Li interaction while Kutzelnigg (K16), within a pseudopotential approach as is utilised here, has indicated that the dipole-quadrupole and quadrupole-quadrupole coefficients are certainly not small in magnitude. The method which will be discussed here is unfortunately not appropriate for the examination of the first of these effects i.e. it cannot be used at short and intermediate internuclear distances. However it is intended to probe the long-range region with some thoroughness with in particular estimates of the R^{-8} and R^{-10} terms being obtained.

* See for example the review by Dalgarno and Davison (D2) for a discussion of theoretical and experimental work prior to 1966.

8.2 Theory and method of solution

A Application of the pseudopotential method

For the systems under investigation i.e. the pairs M–M' at long range, any interactions other than between the valence electrons is neglected. Thus the influence of the atomic cores is only apparent through the model Hamiltonians of which each valence pseudowavefunction is an eigenfunction as in (1).

$$h^{o}(1)\ \psi_{ls}(1) = \varepsilon^{o}_{ls}\ \psi_{ls}(1) \qquad (1)$$

where ψ_{ls} is the ground state valence pseudowavefunction and ε^{o}_{ls} is the one-electron energy (generally set equal to the negative of the ground state I.P.).

As in the previous Chapter the single-particle model Hamiltonian is taken to be ℓ-dependent and is written as (2).

$$h^{o}(1) = -\tfrac{1}{2}\nabla_1^2 + \sum |\ell\rangle v_\ell \langle\ell| \qquad (2)$$

With a total Hamiltonian for the non-interacting atomic subsystems as the sum $h^{o}_{a}(a1) + h^{o}_{b}(b2)$ the zeroth wavefunction is of product form. Thus on application of perturbation theory (3) is obtained in obvious analogy to the equations derived in 6.

$$(h^{o}_{a}(a1) + h^{o}_{b}(b2) - \varepsilon^{o}_{ls_a} - \varepsilon^{o}_{ls_b})\Psi' = -\Sigma H'_{ij}\ \psi_{ls_a}(a1)\,\psi_{ls_b}(b2) \qquad (3)$$

If the h^o are now more fully written down as in (2) the equation (4) is arrived at.

$$\left(-\tfrac{1}{2}\nabla_{a1}^2 - \tfrac{1}{2}\nabla_{b2}^2 + \sum |l_{a1}\rangle V_{l_{a1}} \langle l_{a1}| + \sum |l_{b2}\rangle V_{l_{b2}} \langle l_{b2}| \right.$$

$$\left. - \varepsilon^o_{ls_a} - \varepsilon^o_{ls_b} \right) \psi' = - \sum H'_{ij}\, \psi_{ls_a}(a1)\, \psi_{ls_b}(b2) \qquad (4)$$

Now from the above it is obvious that if the first order wavefunction is expanded customarily in the manner (5) then as before decoupling will occur giving an equation (6) for each pair function ij.

$$\psi' = \sum U_{ij}(r_{a1}, r_{b2})\, \Theta_{ij}\, R^{-i-j-1} \qquad (5)$$

$$\left(-\tfrac{1}{2}\nabla_{a1}^2 - \tfrac{1}{2}\nabla_{b2}^2 + V_{l_i}(r_{a1}) + V_{l_j}(r_{b2}) - \varepsilon^o_{ls_a} \right.$$

$$\left. - \varepsilon^o_{ls_b} \right) U_{ij}(r_{a1}, r_{b2})\, \Theta_{ij}$$

$$= - 4\pi\, M_{ij}\, r_{a1}^i\, r_{b2}^j\, \psi_{ls_a}(a1)\, \psi_{ls_b}(b2)\, \Theta_{ij} \qquad (6)$$

It may be noted at this point that the l-dependent pseudopotentials in (2) give rise to appropriate terms in (6) viz. for the dipole-dipole term, which may be considered as due to simultaneous p-type excitations on each centre, the potentials are $V_p(a1)$ and $V_p(b2)$. It may also be remarked that if the model potential did not contain a repulsive portion preventing penetration into the core then the necessary orthogonalisation of the first order wavefunction to the core orbitals would present very great

problems indeed.

From (6) elementary integration over the angular variables furnishes the radial equations for the components of the first order function.

$$\left(-\tfrac{1}{2}\left(r_{a1}^{-2} \frac{\partial}{\partial r_{a1}} \left(r_{a1}^{2} \frac{\partial}{\partial r_{a1}}\right) + r_{b2}^{-2} \frac{\partial}{\partial r_{b2}} \left(r_{b2}^{2} \frac{\partial}{\partial r_{b2}}\right)\right) + \tfrac{1}{2} \ell_i (\ell_i + 1) r_{a1}^{-2} \right.$$

$$+ \tfrac{1}{2} \ell_j (\ell_j + 1) r_{b2}^{-2} + V_{\ell_i}(r_{a1}) + V_{\ell_j}(r_{b2}) - \varepsilon^{o}_{1s_a}$$

$$\left. - \varepsilon^{o}_{1s_b} \right) U_{ij}(r_{a1}, r_{b2}) = - M_{ij} r_{a1}^{i} r_{b2}^{j} R_{1s_a}(r_{a1}) R_{1s_b}(r_{b2}) \qquad (7)$$

Clearly the equations (7) are easily solved to a high degree of accuracy using the finite-difference approach earlier elucidated, the local model potentials giving a very simple structure to the differential equations. In contrast if a variational method is employed for the solut--ion of (3) or any of the equations leading from it then a considerable amount of effort must be expended in determining suitable radial basis sets for the first order functions to ensure precision (K16). Additionally it is not generally economical to investigate several types of model potential using a variational approach owing to the necessity to reprogram integral routines whereas with the numerical technique it is only required to regenerate the potential and zeroth function column vectors.

B Choice of pseudopotential and numerical procedures

Owing to the simple form of the radial equations for the components of the first order function the use of a wide range of diffe--rent pseudopotentials could be examined. Results are presented here for

the four model potentials employed in the previous Chapter viz.

Type A —— Hellmann potential ;

Type B —— Cutoff potential ;

Type C —— Modified Coulomb approximation ;

Type D —— Gl Atomic Effective Potential ;

It may be observed that in equation (7) potentials apposite to different ℓ are required according as the pair function is U_{11}, U_{12} and so on. Hence for the dipole-dipole (B_6) term only p potentials are required and all the model potentials listed above can be utilised straightforwardly. For the higher order terms though e.g. B_8 for which both p and d potentials are needed, Type C is the only approximation which can easily be applied without further elaborate parameterisation.* For Li however, as has been seen in the polarisability calculations, the p potential can be used for d,f excitations without serious error. For H of course the bare nucleus potential can be used throughout.

The details of the procedures employed for the numerical calculations are very simple:- For any of the approaches the potential and pseudowavefunction vectors could be easily generated from given data as has been described in Chapter 7. For the solution of each of the part--ial differential equations it was generally found sufficient to use 20(5)40 strips in each dimension on a 'square root' grid with a radial

* Alternatively one could say approximate the d potential in Na by the simple Coulombic term -1/r as has been carried out by Kutzelnigg (K16). It is felt though that this rather ad hoc procedure introduces possible errors of unknown magnitude.

cutoff as was determined for the corresponding polarisability computa-
-tion. Application of the Richardson process gave a final accuracy of about five figures in most cases with the possible exception of the Type B (Cutoff) potential for which it was found that extrapolation furnished slightly less precise results. It is believed though that all the quanti-
-ties presented here should be accurate to the number of digits listed.

8.3 Results and discussion

Calculations were performed for all possible 20 pairs M - M', M - H and M - M for the alkali metal atoms Li to Cs. The results for Li-Li and Li-H will first be discussed in some detail as for these pairs there are a number of accurate calculations available for the purposes of comparison. Accordingly in Tables 8.1 and 8.2 for these systems the res-
-ults of the present work are listed for the B_6, B_8 and B_{10} dispersion coefficients together with the values of other workers for these quantities.

For Li-Li it may be observed that all of the model potential methods give values for the B_6 coefficient which differ little, the spread about the median value being only $\pm$ 1½%. In addition they are in harmony with several previous calculations of which probably the most accurate is that of Stacey and Dalgarno (S24) who quote a value of 1391 $\pm$ 28 a.u.. The agreement among the estimates is maintained for the higher order coefficients B_8 and B_{10} with the disparity between the highest and lowest values rising to only 5% in the worst case. It is unfortunately not possible to give a comparison with any non-empirical calculations as no such results appear to have been reported in the literature though Kutzelnigg (K16), using a pseudopotential method, has obtained values for the dipole-quadrupole and quadrupole-quadrupole

Table 8.1 A comparison of values obtained for the Li-Li dispersion coefficients in this work and by others.

	B_6	B_8	B_{10}^a	B_{10}^b	B_{10}^c
Pseudopotential A	0.1390(4)	0.8200(5)	0.4582(7)	0.2630(7)	0.7212(7)
Pseudopotential B	0.1436(4)	0.8533(5)	0.4825(7)	0.2767(7)	0.7592(7)
Pseudopotential C	0.1419(4)	0.8300(5)	0.4627(7)	0.2645(7)	0.7272(7)
Pseudopotential D	0.1409(4)	0.8429(5)	0.4786(7)	0.2737(7)	0.7523(7)
Dalgarno & Davison[d]	0.1380(4)	—	—	—	—
Stacey & Dalgarno[e]	0.1391(4)	—	—	—	—
Kutzelnigg[f]	0.1356(4)	0.84(5)	—	0.28(7)	—

[a] Dipole–octupole term. [b] Quadrupole–quadrupole term. [c] Total B_{10} term.

[d] References (D2, D3). Semi-empirical calculation.

[e] Reference (S24). Non-empirical evaluation based on CI calculation.

[f] Pseudopotential calculation, reference (K16).

Table 8.2 A comparison of values obtained for the Li-H dispersion coeff--icients from this work and by others.

	B_6	B_8	B_{10}^a	B_{10}^b	B_{10}^c
Pseudopotential A	0.6598(2)	0.3236(4)	0.1754(6)	0.4449(5)	0.2199(6)
Pseudopotential B	0.6687(2)	0.3325(4)	0.1832(6)	0.4584(5)	0.2291(6)
Pseudopotential C	0.7451(2)	0.3640(4)	0.1968(6)	0.5002(5)	0.2469(6)
Pseudopotential D	0.6613(2)	0.3281(4)	0.1810(6)	0.4519(5)	0.2261(6)
Dalgarno & Davison[d]	0.65(2)	—	—	—	—
Stacey & Dalgarno[e]	0.6665(2)	—	—	—	—
Kutzelnigg[f]	0.67(2)	0.330(4)	—	0.455(5)	—

[a] Dipole-octupole term. [b] Quadrupole-quadrupole term. [c] Total B_{10} term.

[d] Semi-empirical calculation, references (D2, D3).

[e] Reference (S24). Non-empirical evaluation based on CI calculation.

[f] Pseudopotential calculation, reference (K16).

terms which are very similar to those found here.* The most noticeable feature of these coefficients is quite obviously their very large magnitude, the ratios B_8/B_6 and B_{10}/B_8 being about 60 and 90 respectively. Thus the power series expansion of the interaction energy cannot be expected to be at all reliable for R less than about 15 to 20 a.u. espe--cially if only the dipole-dipole term is retained. Interestingly, but only partly related, there is evidence to suggest that it is for smaller internuclear distances than this that singlet-triplet branching starts to occur (B2, D2, K17). It may finally be noted that as far as the empir--ical determination of B_6 is concerned then the experiments employed must involve only the measurement of properties which depend on the region of the potential for R greater than about 20 a.u. ..... a feature which does not seem to apply to the scattering experiments which have been used in an attempt to determine this quantity for various other alkali metal pairs (B15).

For the Li-H interaction the results for the A, B and D model potential methods are again in good agreement with each other and with previous calculations, all of the estimates for the leading Van der Waals coefficient being within 1% of the accurate value of 66.65 a.u. of Stacey and Dalgarno (S24). Unfortunately for the modified Coulomb approx--imation the results are clearly too large by about 10% though it is not clear at this time which of the assumptions involved in this method is responsible for this inaccuracy. The convergence of the expansion of the interaction energy is about the same as for the Li-Li pair, the ratios

* Kutzelnigg has apparently omitted to evaluate the important dipole-octupole contribution to B_{10}.

B_8/B_6 and B_{10}/B_8 being only about 20% down at about 50 and 70. Hence similar strictures on the range of validity of the perturbation approach apply to this system as for that discussed in the previous paragraph.

Turning to the other pairs full results for the B_6 term for all the alkali metal interactions are listed in Table 8.3 for the first three model potentials, only the diagonal (M - M) terms being computed for the Cutoff potential owing to the awkwardness of the discontinuity in the potential function. Again overall agreement is very good, the only possible discrepancies being for the Coulomb approximation when metal - hydrogen pairs are considered. This view is reinforced by the comparison of the dipole-dipole coefficients evaluated using the Hellmann potential and the semi-empirical results of Dalgarno and Davison (D2, D3),* the two sets of computations differing little as can be seen from Table 8.4.

In Tables 8.5 and 8.6 values are listed for all of the systems studied of the B_8 and B_{10} dispersion coefficients evaluated using the Type C model potential. As stated previously a major objective of this section of the work was to examine these contributions to the interaction energy so as to throw some light on the disagreement between experimental and theoretical estimates of the dipole-dipole coefficient. Broad order-of-magnitude values are thus required rather than very accurate results and hence minor inaccuracies (such as probably occur for the M - H coefficients) are not of consequence for the purpose considered

* Comparison is effected in general with only the valence electron contr--ibutions of Dalgarno and Davison as the present pseudopotential method deals only with this component of the long-range interaction. However core contributions may be quite considerable for the heavier atoms, perhaps 10% or more.

Table 8.3 A comparison of the dipole-dipole dispersion coefficients for the interaction of alkali metal atoms using the model potential approaches described in the text. In each block the first, second and third entries refer to the Type A, B and C potentials respectively.

	Li	Na	K	Rb	Cs
	1390	1465	2333	2549	3065
Li	1436	—	—	—	—
	1419	1470	2308	2512	2993
		1549	2447	2674	3184
Na		1575	—	—	—
		1529	2381	2590	3076
			3937	4301	5189
K			3910	—	—
			3772	4108	4909
				4707	5633
Rb				4589	—
				4474	5350
					6810
Cs					6590
					6411
	65.98	72.22	104.6	113.6	131.7
H	66.87	73.01	104.5	112.6	130.7
	74.51	80.17	111.5	119.3	135.1

Table 8.4 A comparison of present results for the B_6 coefficients for the interaction of alkali metal atoms with the semi-empiri--cal calculations of Dalgarno and Davison (in this Table only the Type A (Hellmann) potential results are included). The estimates of Dalgarno and Davison are valence electron contributions from reference (D3) with the exception of the M — H dispersion coefficients which are from (D2).

	Li	Na	K	Rb	Cs
Li	1390[a]	1465	2333	2549	3065
	1380[b]	1470	2240	2440	3000
Na		1549	2447	2674	3184
		1580	2390	2600	3180
K			3937	4301	5189
			3680	4000	4940
Rb				4707	5633
				4350	5370
Cs					6810
					6660
H	65.98	72.22	104.6	113.6	131.7
	65	73	103	112	137

[a,b] First entry in each block gives the present results while the second refers to those of Dalgarno and Davison.

Table 8.5 The values of the B_8 coefficients for the interaction of alkali metal atoms using the Type C pseudopotential method.

	Li	Na	K	Rb	Cs
Li	0.8300(5)	0.9607(5)	0.1854(6)	0.2182(6)	0.3010(6)
Na		0.1102(6)	0.2080(6)	0.2431(6)	0.3305(6)
K			0.3841(6)	0.4455(6)	0.6003(6)
Rb				0.5148(6)	0.6900(6)
Cs					0.9178(6)
H	0.3640(4)	0.4310(4)	0.7938(4)	0.9141(4)	0.1183(5)

Table 8.6 The values of the B_{10} coefficients for the interaction of alkali metal atoms using the Type C pseudopotential method. In each block the first and second entries refer to the dipole–octupole and quadrupole–quadrupole contributions respectively while the third gives the total coefficient.

	Li	Na	K	Rb	Cs
	0.4627(7)	0.5566(7)	0.1237(8)	0.1501(8)	0.2167(8)
Li	0.2645(7)	0.3269(7)	0.7017(7)	0.8428(7)	0.1185(8)
	0.7272(7)	0.8835(7)	0.1939(8)	0.2344(8)	0.3352(8)
		0.6598(7)	0.1413(8)	0.1699(8)	0.2417(8)
Na		0.4046(7)	0.8744(7)	0.1053(8)	0.1487(8)
		0.1064(8)	0.2287(8)	0.2752(8)	0.3904(8)
			0.2772(8)	0.3263(8)	0.4485(8)
K			0.1947(8)	0.2367(8)	0.3417(8)
			0.4719(8)	0.5933(8)	0.7902(8)
				0.3818(8)	0.5195(8)
Rb				0.2887(8)	0.4200(8)
				0.6705(8)	0.9395(8)
					0.6951(8)
Cs					0.6222(8)
					0.1317(9)
	0.1968(6)	0.2526(6)	0.6104(6)	0.7457(6)	0.1072(7)
H	0.5002(5)	0.6009(5)	0.1141(6)	0.1321(6)	0.1722(6)
	0.2469(6)	0.3126(6)	0.7245(6)	0.8778(6)	0.1245(7)

Table 8.7 A comparison of the present pseudopotential results (from the Type C method) with those of Kutzelnigg (K16) for the B_8 and B_{10}^b coefficients of the diagonal (M — M) interaction of alkali metal atoms.

	This work	Kutzelnigg
B_8		
Li-Li	0.8300(5)	0.840(5)
Na-Na	0.1102(6)	0.120(6)
K-K	0.3841(6)	0.400(6)
Rb-Rb	0.5148(6)	0.530(6)
Cs-Cs	0.9178(6)	0.880(6)
B_{10}^b		
Li-Li	0.2645(7)	0.28(7)
Na-Na	0.4046(7)	0.43(7)
K-K	0.1947(8)	0.204(8)
Rb-Rb	0.2887(8)	0.288(8)
Cs-Cs	0.6222(8)	0.540(8)

[b] Quadrupole-quadrupole term.

here. Nevertheless the stated results probably do not differ by more than about 10% from the true B_n, this being partly confirmed by the comparison with the work of Kutzelnigg (K16) given in Table 8.7, agreement being surprisingly good despite the before mentioned approximations used by this author. As for Li-Li it is apparent that for all of the systems the higher order terms are very large and hence will be of importance even at fairly large internuclear distances. For example for the Cs diagonal pair at 25 a.u. the B_8 and B_{10} terms still contribute no less than 22% of the sum $\Sigma B_n R^{-n}$ through B_{10} while even at 40 a.u. these effects pers--ist to a significant 10% of the energy sum. To conclude it is thus scarcely surprising with this evidence that the interpretation of empiri--cal data on the assumption of the dipole-dipole term in the long-range interaction energy leads to values of B_6 which are at variance with theoretical estimates. Further experimental work would thus appear to be desirable.

8.4 Conclusions

In this Chapter it has been seen how semi-empirical techni--ques can be straightforwardly applied using the finite-difference approach to the evaluation of long-range interactions introduced earlier in this Thesis. Clearly the method can be fairly easily extended especia--lly if only local potentials are involved and the work presented here must be regarded as being in an early stage of development. Not only does it seem possible to contemplate the determination of long-range interact--ions between systems other than those containing a single valence electron but there does not appear to be any reason why the method cannot be used

successfully for the calculation of three-body forces, the leading term of which appears in the third order of perturbation theory (D2).* This topic is actively under investigation.

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* Cf. the composition of second and third order energy terms in electron pair correlation calculations of the type carried out earlier. See Chapter 3 and appropriate references contained therein.

Chapter 9 The Numerical Calculation of Pair Energies in Many-Electron Systems: Semi-Empirical Methods.

9.1 Introduction

In this final Chapter before the Summary some work which is in an early, but interesting, stage of development will be reported. Here it is intended to relate some calculations of valence pair energies and ionisation potentials using a combination of the model potential methods employed in the previous two Chapters and of the type of numerical techniques used in 2 and 3, though within a non-perturbation framework.

The underlying idea of this section is to compute in an accurate manner correlated wavefunctions for valence electron pairs in various atomic systems, the effect of the core being represented by one-electron model potentials.* Hence it is hoped that this allowance for correlation in the valence shell will yield improved values for chemically interesting quantities without leading to an excessively complicated calculation. Such a concept of moving beyond the Hartree-Fock model by allowing for correlation between the outer electrons only is certainly not new with probably the earliest definitive analysis being given by Fock, Vesselov and Petrashen (F2) who demonstrated the necessary orthog--onality constraints to prevent "the nightmare of the inner shells". Similar early suggestions appear also to have been made by others as is

* Perhaps a less arbitrary alternative, but in a similar spirit to this work, is presented by either the method of Weiss (W7) or that of Szasz and McGinn (S28, S31), the latter being based on Phillips-Kleinman (P5) potentials.

reviewed by Hartree (H3). However it is with the development of the pseudo or model potential method as a means of eliminating the orthogonality problem that such calculations have become tractable for many systems, results being reported by several workers notably Szasz and McGinn (S28, S30, S31), Weeks and Rice (W4) and Schwartz (S13, S15).

Generally variational techniques have been used in the studies referred to above with either a Hylleraas or CI trial wavefunc-tion. Unfortunately the determination of a suitable basis set of two-particle functions is no small difficulty (see e.g. references (W4, W5)) and it is not easy to ascertain whether variational convergence has been achieved for any particular problem. Thus, as will be demonstrated, the encouraging results recorded by some workers appear to be due to a fortuitous cancellation of error consequent on a rather severe limita-tion of the number of terms in the pair pseudowavefunction. Accordingly it is here intended to remove this deficiency by solving accurately for the function in question by a numerical process which is strictly equiva-lent to CI.

The systems chosen for investigation are those atoms having a single s^2 pair of electrons outside a closed core e.g. the ground states of Mg, Ca, K^-. Model potentials of the Hellmann and Cutoff types are employed for the calculations which have the purpose of demonstrating both the feasibility and accuracy of the numerical procedures and of the practicability of the pseudopotential approach. In particular its predic-tive ability will be tested on the interesting problem of the determin-ation of the electron affinities of the alkali metals.

9.2 Derivation of the effective pair equation and method of solution

A Derivation of the equation for the valence pair

The effective equation for the valence electron pair will now be derived following the treatment of Weeks and Rice (W4), the type of system being considered consisting of an atom having a pair of electrons outside a closed core of N orbitals.

Fock, Vesselov and Petrashen (F2) have demonstrated that the wavefunction for an $N + 2$ electron system can be approximated as (1)

$$\Phi = A_n(\Psi(N+1,N+2) \times A(\prod_{i=1}^{N} \Phi_i(i))) \qquad (1)$$

where A_n suitably normalises and antisymmetrises the total wavefunction and $\Psi(N+1,N+2)$ is a correlated function for the valence pair subject to the condition of being one electron orthogonal to the core orbitals i.e.

$$\int \Psi(1,2)\ \Phi_c(1)\ d\tau_1 = \int \Psi(1,2)\ \Phi_c(2)\ d\tau_2 = 0 \qquad (2)$$

With a wavefunction of the form (1) the total energy for the atom can be expressed as in (3):-

$$E \geq E_{true} = \int \Psi(1,2)\ (h^o(1) + h^o(2) + r_{12}^{-1})\ \Psi(1,2)\ d\tau_1\ d\tau_2 + E_c \qquad (3)$$

or

$$E = E_{12} + E_c \tag{4}$$

where in the above equations $h^o(i)$ is a one-electron HF operator defined with respect to the core orbitals in (1) and E_c is the energy of the core. It may be noted that E is an upper bound to the energy of the atom regardless of the choice of core and valence functions provided the orthogonality constraints (2) are satisfied.

If the one-electron projection operator over the core space of electron i is defined as in (5) then clearly (6) is a suitable function for the valence pair, Φ being a general non-orthogonal pair function.*

$$P_i = \sum_{c=1}^{N} |\Phi_c(i)\rangle \langle\Phi_c(i)| \tag{5}$$

$$\Psi(1,2) = (1 - P_1)(1 - P_2)\Phi(1,2) \tag{6}$$

Now, as shown by Weeks and Rice, the minimisation of (7) subject to the overall normalisation condition (8) furnishes the two-particle equation for the valence pair function (9).

$$F_{12} = \langle (1 - P_1)(1 - P_2)\Phi | H | (1 - P_1)(1 - P_2)\Phi \rangle \tag{7}$$

* Cf. orthogonality constraints discussed in Chapter 3.

$$\langle (1 - P_1)(1 - P_2)\Phi \mid (1 - P_1)(1 - P_2)\Phi \rangle = 1 \qquad (8)$$

$$(1 - P_1)(1 - P_2)(h^{\circ}(1) + h^{\circ}(2) + r_{12}^{-1} - E_{12})(1 - P_1)(1 - P_2)\Phi(1,2) = 0 \qquad (9)$$

The energy of the valence pair can be written as (10) where ε_1, ε_2 is the energy of the valence electron in the corresponding $N + 1$ electrom system and ε_{12} is the "interaction" energy between the two valence electrons.

$$E_{12} = \varepsilon_1 + \varepsilon_2 + \varepsilon_{12} \qquad (10)$$

Noting that $(1 - P_i)$ is idempotent and commutes with $h^{\circ}(j)$ where $i \neq j$ then (9) can be rearranged to (11).

$$\begin{aligned} (\; & ((1 - P_1)(h^{\circ}(1) - \varepsilon_1)(1 - P_1))\,(1 - P_2) \; + \\ & ((1 - P_2)(h^{\circ}(2) - \varepsilon_2)(1 - P_2))\,(1 - P_1) \; + \\ & (1 - P_1)(1 - P_2)(r_{12}^{-1} - \varepsilon_{12})(1 - P_1)(1 - P_2) \;)\Phi(1,2) = 0 \end{aligned} \qquad (11)$$

The projection operators anf the HF single-particle operators should be applied using the core orbitals of the $N + 2$ electron atom but however there is probably little error in replacing them with those for the $N + 1$ electron system. This done it may be seen that it is reasonable to further approximate terms such as $(1 - P_1)(h^{\circ}(1) - \varepsilon_1)(1 - P_1)$ by

$h^m(1) - \varepsilon_1$ where $h^m(1)$ is a one-electron model Hamiltonian for the single valence electron system of the type (12) introduced in Chapters 7 and 8.

$$h^m(1) = -\tfrac{1}{2}\nabla_1^2 + \Sigma\, |\ell_1\rangle\, v_{\ell_1} \langle\, \ell_1| \qquad (12)$$

Introduction of the model potentials thus furnishes the equation (13) for the pair function.

$$((h^m(1) - \varepsilon_1)(1 - P_2) + (h^m(2) - \varepsilon_2)(1 - P_1) +$$
$$(1 - P_1)(1 - P_2)(r_{12}^{-1} - \varepsilon_{12})(1 - P_1)(1 - P_2))\, \phi(1,2) = 0 \qquad (13)$$

The projection operators are unfortunately not entirely eliminated from the pair equation by the introduction of the model potentials and, although some very accurate calculations have been carried out within this framework by Weeks and Rice (W4), the theory is still somewhat complicated for general usage. Hence the pair equation which will be employed in this work is (14) which arises when the remaining projection operators are ignored.

$$(h^m(1) + h^m(2) - \varepsilon_1 - \varepsilon_2 - \varepsilon_{12})\, \phi(1,2) = 0 \qquad (14)$$

This reduction of (13) to (14) represents an important simplification in two ways viz. it eliminates the awkward problem of defining a set of core orbitals and also it gives an equation which is clearly computationally

much more tractable. On physical considerations it is felt that such an approximation should not lead to errors of any greater magnitude than those introduced already by the various assumptions leading to (13) since there should only be substantial differences between results from the two methods when there is substantial penetration of the valence wave--function into the core. The repulsive form of the pseudopotentials within this region should prevent this occuring to any appreciable extent and hence it might be expected that (14) should give reasonable values for valence pair energies, this aspiration being supported by the previous encouraging results of several workers (W4, W5, S13, S15).

B Reduction to radial form and method of solution

To reduce the equation (14) to a form which is suitable for the application of numerical methods it is convenient to expand the pair function as in (15).

$$\phi(1,2) = \sum_{\ell=0}^{\infty} U_\ell(r_1,r_2)\ (4\pi)^{-1}\ (2\ell+1)^{\frac{1}{2}}\ P_\ell(\cos\Theta_{12}) \qquad (15)$$

Now insertion of this wavefunction in the model pair equation with ℓ-dependent potentials (12) yields on manipulation and integration over the angular variables the infinite set of coupled partial differential equations (16).*

* The derivation of such equations for He like systems appears to have been first carried out by Lennard-Jones and Pople (L7).

$$\left(-\tfrac{1}{2}\left(r_1^{-2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1}\right) + r_2^{-2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2}\right)\right) + \tfrac{1}{2}\ell(\ell+1)\, r_1^{-2} \right.$$

$$\left. + \tfrac{1}{2}\ell(\ell+1)\, r_2^{-2} + V_\ell(r_1) + V_\ell(r_2) + M^k(\ell,\ell)\right) U_\ell(r_1,r_2)$$

$$= E \times U_\ell(r_1,r_2) - \sum_{\ell' \neq \ell} M^k(\ell',\ell)\, U_{\ell'}(r_1,r_2) \qquad (16)$$

where

$$M^k(\ell',\ell) = c^k(\ell',\ell) \frac{r_<^k}{r_>^{k+1}} \qquad (17)$$

and

$$c^k(\ell',\ell) = \tfrac{1}{2}(2\ell'+1)^{\frac{1}{2}} (2\ell+1)^{\frac{1}{2}} \times \int P_{\ell'}(\cos\Theta_{12})\, P_k(\cos\Theta_{12})\, P_\ell(\cos\Theta_{12})\, d(\cos\Theta_{12}) \qquad (18)$$

The above are merely the pseudopotential analogues of the 'exact' pair equations solved numerically for two-electron systems by McKoy, Winter and co-workers (W12, W14, W15). They are completely equiv--alent to CI, the truncation of the wavefunction after one, two terms being identical to the inclusion of only ss' or ss' and pp' configura--tions in the two cases respectively. This is perhaps emphasised by not--ing that the pseudopotentials occurring in the first equation are those appropriate in the one-electron model system to states of s symmetry while for the second, third ..... p,d ..... potentials are present.

For the systems under study it was decided to truncate the expansion of the wavefunction (15) after only two terms. There is ample evidence that for the species upon which the calculations were carried out the correlation energy of the valence shell is very largely given by

the s^2 — p^2 near-degeneracy effect (see for example references (A8, A9, L9, M3, M4, T4) and also the work of Chapter 3) and hence the contribut-ion of d and higher excitations is inconsequential for the purposes of this work. Neither is it felt that the inclusion of such small additions to the pair energy will be significant in comparison to the approximations involved in introducing the model potentials into the equation for the pair function.

There are though no approximations required in the solution of the coupled equations (16), the structure of the latter being partic-ularly favourable for rapid numerical resolution: A similar scheme was adopted to that employed for the eigenvalue problems arising in Chapter 4 when the calculation of single-centre molecular wavefunctions was considered i.e. the equations were solved first for the simpler one term S limit wavefunction and then this was used as an initial approximation for the pair of coupled equations. The linear equations arising on replacement of the second derivatives by appropriate finite-difference approximations were found to be soluble using SOR* owing to the repulsive form of the model potentials in the core region thus giving fairly modest computational requirements. Using fourth difference finite-difference formulae 20(5)35 strips on a 'square root' grid was usually found adequate to give 5 to 6 figure accuracy in the pair energies on application of the Richardson process, only exceptionally finer spacing being required, notably with the 'cutoff' potential. As a check on the accuracy of the program it was found that for a wide range of radial

* This is not generally true for bare nucleus or other such potentials as the finite-difference matrix is not necessarily diagonally dominant. It is however fortuitously so for the example of H^-.

cutoffs and grid sizes the S and P limits of the hydride ion given by Winter (W13) as -0.51499 and -0.52658 a.u. could be reproduced within 0.00001 — 0.00002 a.u. with little difficulty. For example a 30.0 a.u. cutoff with 25(5)45 strips in each dimension gave -0.514497 and -0.526597 a.u. respectively for the S and P limits of H^-.

Calculations were performed for a wide range of systems using the Type A (Hellmann) and Type B (Cutoff) potentials described in previous Chapters. However before the discussion of the results one may note the necessity of utilising an accurate method of solution of (14) to ensure that erroneous conclusions are not drawn from computed results. In Table 9.1 some results are given for the pair energies of a number of atoms as calculated by Szasz and McGinn (S30) and by the writer using the present numerical procedures but retaining the same Hellmann potentials as these workers.* It is apparent that when the pair energies are accurately comp--uted they are found to exceed substantially both the values of Szasz and McGinn and the experimental results. Thus the apparently encouraging computations of these authors seem to be entirely a consequence of their inadequate selection of variational trial functions, highlighting the need to determine the pair functions accurately by either exhaustive variational calculations or by a numerical process as here.

9.3 Discussion

In Table 9.2 results for the alkaline earths are reported using the two different model potentials together with the HF pair

* The deficiencies of the parameterisation of this version of the Hellmann potential have already been remarked on in Chapter 7.

Table 9.1 A comparison of pair energies obtained using the Szasz and McGinn (S30) parameters for the Hellmann potential. All energies are in eV.

System	S limit[a]	P limit[a]	Szasz & McGinn[b]	Experimental[c]
Mg	24.9	25.6	22.67	22.67
Ca	19.0	19.7	17.78	17.98
Sr	16.9	17.5	16.25	16.72
Na^-	5.66	6.01	—	5.68
Zn	29.9	30.7	27.30	27.35
Cd	27.8	28.5	25.55	25.90

[a] This work, numerical CI method.

[b] CI variational wavefunction, reference (S30).

[c] Taken from experimental data compiled by Moore (M7) with the exception of Na^- for which the pair energy is estimated from the SOC calculation of Weiss (W7).

Table 9.2 Pair energies, ionisation potentials computed using the Type A, Type B potentials compared with Hartree-Fock results and experimental data. All energies are in eV.

	Be	Mg	Ca	Sr	Ba	Ra
Type A model potential						
S limit pair energy	26.36_5	21.79_6	17.24_9	16.03_6	14.55_3	14.74_9
P limit pair energy	27.57_8	22.66_2	18.01_5	16.73_1	15.20_3	15.35_5
Ionisation potential	9.37	7.63	6.14	5.70	5.20	5.22
Type B model potential						
S limit pair energy	25.90_7	21.46_7	16.95_5	15.70_5	14.21_9	14.40_0
P limit pair energy	27.19_2	22.31_2	17.68_8	16.35_9	14.82_1	14.94_4
Ionisation potential	8.98	7.28	5.82	5.33	4.82	4.80
HF pair energy[a]	26.169	21.327	16.447	—	—	—
Ionisation potential	8.05	6.61	5.12	—	—	—
Experimental pair energy[b]	27.52_6	22.67_4	17.98_1	16.71_9	15.21_1	15.42_1
Ionisation potential	9.320	7.644	6.111	5.692	5.210	5.277

[a] Evaluated from work of Clementi (C7).

[b] Sum of first and second ionisation potentials from Moore (M7).

energies and ionisation potentials and also relevant experimental data. It is immediately observable that both pseudopotential methods yield a substantial improvement over the HF model. This is of course largely a consequence of incorporating experimental data in the potentials such that the correct energies are reproduced for the N + 1 electron systems but nevertheless the major elements of the pseudo two-electron system are reproduced to a surprising degree. For example, assuming that the correl--ation energy of the ns^2 pair is given predominantly by the s^2— p^2 near-degeneracy effect, for Be the Type A and Type B potentials give E_{corr} of 1.21 and 1.29 eV which may be compared with a probable $2s^2$ pair correlation energy of 1.23 — 1.25 eV (see Chapter 3). Similarly for Mg the respective increments for the model problem are 0.87 and 0.85 eV which may be compared with the estimate of McKoy and Sinanoglu (M3, M4) of 0.83 eV and of Nesbet (N4) of 0.92 eV.

It is evident though from the Table that the 'cutoff' potential results are somewhat inferior to those obtained using the Hellmann potential. In part this is of course purely fortuitous as one cannot expect extreme accuracy from such a simplified model and in part it is perhaps due to the neglect of the projection operators when approxima--ting (13) as (14). (The effect of the latter requires further investig--ation though, as demonstrated by Weeks, Hazi and Rice (W5), it is unlik--ely to be very important provided one obtains an accurate approximation to the exact solution of (14).*) However it does appear that the rather

* The ad hoc procedure of Simons (S16) of multiplying the r_{12}^{-1} term by a screening factor to allow for this neglect of projection operators seems undesirably arbitrary and is probably unnecessary.

Table 9.3 A comparison for the isoelectronic sequence Li^- to F^{5+} of results using the Hellmann potential with those obtained from other methods. All energies are in eV.

	Li^-	Be	B^+	C^{2+}
S limit	5.48_3	26.36_5	61.50_5	110.46
P limit	6.00_5	27.57_8	63.21_6	112.63
I.P.	0.61_5	9.37	25.29	48.14
H.F. pair energy[a]	5.219	26.169	61.259	110.127
I.P.	-0.12	8.05	23.45	45.78
Ab initio I.P.[b]	0.47	9.10	24.86	47.50
Experimental pair energy[c]	6.01	27.52_6	63.06_9	112.34
I.P.	0.62	9.32	25.15	47.86

	N^{3+}	O^{4+}	F^{5+}
S limit	173.11	249.45	339.47
P limit	175.73	252.51	342.98
I.P.	77.85	114.41	157.81
H.F. pair energy[a]	172.678	248.876	338.705
I.P.	74.98	111.01	153.86
Ab initio I.P.[b]	77.01	113.35	156.52
Experimental pair energy[c]	175.31_3	251.95_3	342.25_6
I.P.	77.45	113.87	157.12

[a] From reference (C7). [b] From work of Chapter 3. [c] Taken from Moore (M7) except for Li^- for which data is estimated from the work of Weiss (W7).

Table 9.4 A comparison for the isoelectronic sequence Na^- to Cl^{5+} of results obtained using the Hellmann potential with those from other sources. All energies are in eV.

	Na^-	Mg	Al^+	Si^{2+}
Hellmann potential				
S limit	5.22_8	21.79_6	46.21_1	77.43_2
P limit	5.67_4	22.66_2	47.28_6	78.67_7
I.P.	0.53_5	7.63	18.84	33.54
H.F. pair energy[a]	4.840	21.327	45.551	76.584
I.P.	-0.11	6.61	17.52	31.95
Experimental pair energy[b]	5.68	22.67_4	47.26_3	78.59
I.P.	0.54	7.644	18.823	33.46

	P^{3+}	S^{4+}	Cl^{5+}
Hellmann potential			
S limit	115.14	159.22	209.78
P limit	116.56	160.76	211.46
I.P.	51.53	72.71	97.17
H.F. pair energy[a]	114.099	157.940	208.019
I.P.	49.68	70.60	94.67
Experimental pair energy[b]	116.3_{61}	$160._5$	$211._0$
I.P.	51.3_{54}	$72._5$	$96._7$

[a] From reference (C7). [b] From Moore, reference (M7) with the exception of Na^- for which data is estimated from the work of Weiss (W7).

inflexible and unphysical nature of the Type B potential in the core region furnishes rather less satisfactory results than for the Hellmann potential. This is maintained uniformly for other species with the cutoff potential giving a typical error of 1 - 2% in the pair energy, though in all cases superiority over the HF model appears to be maintained. The Hellmann potential computations are though of continuing accuracy even surprisingly for highly charged ions as can be seen from Tables 9.3 and 9.4 in which full results are reported for the Be and Mg isoelec--tronic sequences. Particularly one may note the comparison of the I.P.s of the members of the Be series computed from the model work and from the Hartree-Fock perturbation theory calculations of Chapter 3, it being evident that for only the most positive species are the ab initio results more accurate than the naive semi-empirical estimates. Additiona--lly for both series the near-degeneracy effect is well represented with as expected the energy increment increasing almost linearly with Z (A8, A9, L9, M3, M4) as can be observed from Figure 9.1 in which the Hellmann potential results are plotted. This can also be observed from Table 9.5 in which data from both model potential methods is compared with the work of McKoy and Sinanoglu (M3, M4) on the Mg sequence.

The above work, although being of academic interest, unfort--unately suffers from the deficiency that one is calculated quantities such as ionisation potentials which have often been determined experimen--tally to a greater degree of precision than the spectral data used for the parameterisation process. It is thus of interest to attempt to predict some properties using the model potential method which are known with considerably less certainty viz. the electron affinities of the alkali metals. In Table 9.6 electron affinities are reported for these systems from Li to Cs as computed using the Type A and Type B potentials together with a variety of theoretical and experimental estimates of these quanti--ties. For Li, as discussed in Chapter 3, all of the various calculations

Figure 9.1

A comparison of the s^2 — p^2 near-degeneracy effect for the Be and Mg isoelectronic sequences, the upper series corresponding to the former. Energies are in eV with the sequence running from M^- ($Z_{eff} = 1$) to M^{5+} ($Z_{eff} = 7$).

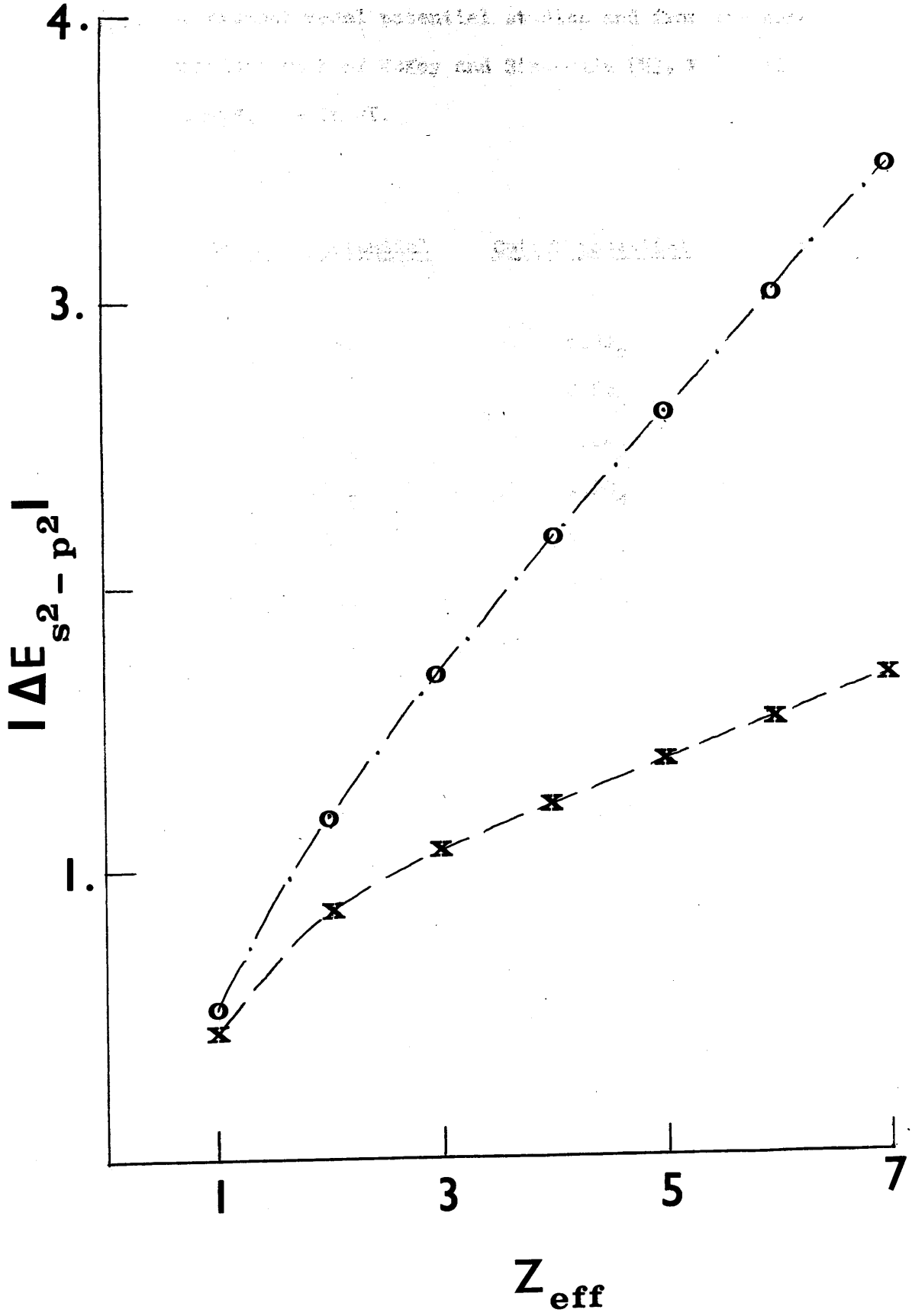
4.
3.
1.
$|\Delta E_{s^2-p^2}|$
1
3
5
7
Z_{eff}

Table 9.5 A comparison of the $3s^2$ — $3p^2$ near-degeneracy effect from the present model potential studies and from the non-empirical work of McKoy and Sinanoglu (M3, M4). All energies are in eV.

System	Hellmann potential	Cutoff potential	McKoy & Sinanoglu
Na^-	0.44_6	0.44_2	—
Mg	0.86_6	0.84_5	0.832
Al^+	1.07_5	1.04_4	1.031
Si^{2+}	1.24_5	1.20_8	1.170
P^{3+}	1.39_8	1.35_7	1.25_9
S^{4+}	1.54_3	1.49_4	1.36_5
Cl^{5+}	1.68_5	1.63_7	1.48_8

Table 9.6 A comparison of values for the electron affinities of the alkali metals from this work and from that of others. Energies are in eV.

	Li	Na	K	Rb	Cs
Type A potential	0.61_5	0.53_5	0.49_8	0.47_7	0.46_0
Type B potential	0.54_8	0.43_6	0.40_1	0.38_3	0.37_2
Hartree-Fock[a]	-0.12	-0.11	-0.07	-0.05	—
Schwartz (S15)	0.62	0.54	0.51	0.48	—
Weiss (W7)	0.61_5	0.53_9	0.46_8	(0.42)	(0.39)
Clementi (C5)	0.58	0.78	0.90	—	—
Victor & Laughlin (V2)	0.59	—	—	—	—
Szasz & McGinn (S31)	0.57	0.49	0.55	0.53	—
Extrapolation[b]	—	—	0.40	0.40	0.40
Experimental[c]	0.6		0.35-0.75	0.20-0.73	0.19-0.70
	0.65-1.05	0.35	0.3	0.27	

[a] Taken from Clementi (C7) except for Rb^- for which results are taken from reference (S31).

[b] From Zollweg, reference (Z1).

[c] Li data is from Ya'Akobi (Y1) and from Scheer and Fine (S3). For other metals results are from Lee and Mahan (L6) and from Smirnov (S22).

suggest an electron affinity of about 0.6 eV in accord with the experim--ental value of Ya'Akobi (Y1). The Hellmann potential result is in harmony with this indicating an electron affinity of about 0.62 eV though the Type B calculations give a somewhat lower result of 0.55 eV. However crudely extrapolating the error in the pair energies for the rest of the again yields, rather fortuitously, an affinity of 0.62 eV. For the other alkali metals there is however rather more disagreement over the values of this quantity (see for example discussions with appropriate references in (W7, S15, Z1)). The present results however suggest a monotonic decrease in the electron affinity as one proceeds down the Column of the Periodic Table in accord with the refined calculations of Weiss (W7) for Li, Na and K, this author giving extrapolated estimates for Rb and Cs. Given the general accuracy displayed for systems such as the alkaline earths for which ionisation potentials are accurately known it is specu--lated that the Hellmann potential electron affinities for Li to Cs of 0.62, 0.54, 0.50, 0.48 and 0.46 eV are unlikely to be gravely in error,* this being in part supported by the cutoff potential calculations. The latter, once roughly corrected for the deficiencies of the approach as for Li, imply electron affinities of about 0.62, 0.53, 0.48, 0.48 and 0.48 eV in good agreement with the other results.

Finally for Cu and Ag the Hellmann potential method gives electron affinities of 0.67 and 0.66 eV respectively. Now for this part of the Periodic Table, as is well-known (S13, S15, S30), the pseudo--potential approach is somewhat less satisfactory than for say the alkali metals. Nonetheless, estimating possible errors in the affinities from calculations on adjacent systems e.g. Zn, Cd, it would seem

* These are naturally in good agreement with Schwartz's results (S15) as similar parameterisation is used.

that these are not likely to be more than 0.8 - 0.9 eV for both cases in complete accordance with the results of Schwartz (S15) for Cu and Szasz and McGinn (S31) for Cu and Ag, the latter employing Phillips-Kleinman potentials. However other workers, notably those using extrapolation techniques, suggest electron affinities of the order of 2. eV i.e. about 2 or 3 times as large (C5, Z1). A thorough examination of this question would thus appear desirable.

9.4 Conclusions

In this Chapter it has been seen how numerical techniques can be efficiently combined with semi-empirical methods so as to calculate correlated valence pair functions to a reasonable degree of accuracy. Clearly much remains to be investigated even before one considers exami--ning configurations other than the s^2 pairs studied here e.g. the the neglect of the projection operators implicit in taking (14) rather than (13) as the model pair equation. In particular it seems likely that rather more attention will have to be paid to the form of the potential in the core region than was apparent in this Chapter. However whether such refining of the potential to include for example core-polarisation effects will have a beneficial result is possibly arguable. Instead one may rather destroy a fortunate cancellation of errors due to the many neglec--ted factors in a valence pair only calculation.

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* For example in the model potential approach no explicit regard is paid to core/valence shell correlation which is by no means small (N4).

Chapter 10 Summary and Conclusions

In this thesis it has been attempted to demonstrate the manner in which simple numerical methods can be used to advantage in the calculation of atomic and molecular properties. Deliberately a fairly wide canvas has been covered in the work to show what is probably the principal advantage of this type of approach, namely the ease by which a liberal selection of problems can be solved owing to the flexibility and simplicity of the finite-difference techniques employed.

As far as future work is concerned several possible extens--ions and new applications have been outlined at various points in the preceding Chapters. Broadly though it is the opinion of the author that versatile and readily applicable techniques such as are used here will increasingly be utilised in preference to more specialised methods as the power of computers grows. In particular when it becomes practicable to solve three-dimensional partial differential equations to the precision achieved here for two-dimensional calculations then the reso--lution of a very large number of quantum chemical problems will be within sight.

Quantum chemistry cannot be described as an 'easy' subject. Neither is the solution of the various differential equations arising in it a trivial matter. Hence it is hoped that the present approach, by its simplicity and general accuracy, will be of assistance as we try to move towards an understanding of our world.

Work continues.

Ronald F. Stewart

Spring 1973

Addenda and Corrigenda

Addendum: Chapter 4

Since the writing of Chapter 4 some very accurate 'exact' results have been obtained from Dr. J.D.Power of the National Research Council of Canada. A comparison for a number of states at R_{ab} = 2.0 a.u. of the present results with the revised data is given below:-

State	Best eigenvalue	Extrapolant	Exact
$1s\ \sigma_g$ *	-1.102112	-1.10256	-1.1026342
$2s\ \sigma_g$	-0.360682	-0.360839	-0.3608649
$3s\ \sigma_g$	-0.177623	-0.177673	-0.1776810
$2p\ \sigma_u$	-0.666499	-0.66744	-0.6675344
$3p\ \sigma_u$	-0.255210	-0.255394	-0.2554132
$3d\ \sigma_g$	-0.235758	-0.235779	-0.2357776
$4f\ \sigma_u$	-0.126644	-0.126644	-0.1266439
$3p\ \pi_u$	-0.20086470	-0.20086483	-0.200864830
$4d\ \pi_g$	-0.12671011	-0.12671014	-0.126710131

* Results from 7 term expansion (Others for σ states are from five term wavefunctions). Values for the $1s\ \sigma_g$ state using a five term expansion are -1.101264 and -1.10245 a.u..

The above results confirm the high accuracy of the one-centre method for the more excited states. Further high precision data is given in Madsen and Peek, reference (M1).

Addendum: Chapter 4

Preliminary calculations have now been carried out for the lowest π state of one-electron diatomic molecules using one of the nuclei as the expansion centre. These indicate that indeed cusp formation at a nucleus is a key factor in the slow convergence of the single-centre method. Results are given below for the off-centre hydrogen atom with the expansion centre at 0.5 a.u. from the H nucleus.

P limit	-0.123064454
D limit	-0.124935150
F limit	-0.124995861
G limit	-0.124999318
H limit	-0.124999802
I limit	-0.124999923
J limit	-0.124999965
Extrapolant	-0.125000006

It can be observed that convergence is very rapid for this calculation and it may be noted that extrapolation assuming an l^{-6} terminal rate yields an inaccuracy of only 1 part in 20 000 000.

Addendum: Chapter 5

Some calculations have been carried out to determine the frequency-dependent polarisability of Be employing the SCPHF method as in Chapter 5 but using Clementi's five term representation of the Hartree-Fock orbitals rather than the six term basis as before. A compar--ison of the two sets of calculations together with the results of Kaveeshwar et al (K6) is given below.

Wavelength (Å)	This work[a]	This work[b]	Kaveeshwar et al
∞	45.566	45.622	45.624
3024.0	161.94	159.79	160.33
2903.0	208.04	204.18	204.39
2791.0	296.46	287.74	286.44
2688.0	521.05	500.83	491.94
2502.0	-789.03	-852.95	-946.77

[a,b] Results computed using the 5 and 6 term basis sets respectively.

The above results indicate that for Be the neglect of the intershell coupling terms in the SCPHF method is probably inconsequential in comparison to the effect of inaccuracies in the zeroth function.

Addendum: Chapters 6 and 8.

The finite-difference approach to long-range interactions has now been extended to three-body forces.

For the long-range interaction of three atomic systems the leading non-additive contribution is expressible as (1) as shown by Dalgarno and Davison (D2).[1]

$$E3(A,B,C) = \nu(A,B,C)\,(1 + 3\cos\Theta_A \cos\Theta_B \cos\Theta_C)\, R_{AB}^{-3} R_{BC}^{-3} R_{CA}^{-3} \qquad (1)$$

Now in terms of the interatomic pair functions the coefficient (A,B,C) can be evaluated as (2) for three identical one-electron atoms.

$$\nu(A,B,C) = \int U_{11}(r_{a1},r_{b2})\, R_{1s}(r_{c3})\, r_{b2}\, r_{c3}\, U_{11}(r_{c3},r_{a1})\, R_{1s}(b2) \times r_{a1}^2\, r_{b2}^2\, r_{c3}^2\, dr_{a1}\, dr_{b2}\, dr_{c3} \qquad (2)$$

For three hydrogen atoms this yields a value of 21.642464_2 a.u. using 20(5)50 strips on a 'square root' grid as for the two-body calculations, the result being in harmony with that of Chan and Dalgarno of 21.6425 a.u.[2] Results for other systems will be given elsewhere as will the extension to 'non-diagonal' interactions.

[1] For earlier studies of this problem see references in Dalgarno and Davison review.

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